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PHYSICO-CHEMICAL MODEL OF TOXIC SUBSTANCES IN THE GREAT LAKES

by

Robert V. Thomann

and

Dominic M. Di Toro

Manhattan College
Environmental Engineering and Science

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Project Officer

William L. Richardson
Large Lakes Research Station
Environmental Research Laboratory - Duluth
Grosse Ile, Michigan 48138

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16. ABSTRACT

A physico-chemical model of the fate of toxic substances in the Great Lakes is constructed from mass balance principles and incorporates principal mechanisms of particulate sorption-desorption, sediment-water and atmosphere-water interactions, and chemical and biochemical decay. Calibration of the toxic model is through comparison to plutonium-239 data collected in the 1970s using a 23 year time variable calculation and indicates that in general, the sediments are interactive with the water column in the Great Lakes through resuspension andoor horizontal transport. Fifty percent response times of ^{239}Pu following a cessation of load extend beyond 10 years with sediment resuspension.

The calibration model was applied to polychlorinated biphenyl (PCB) using a high and low estimate of contemporary external load and with and without volatilization. The results of the application using a 20 year calculation indicate that a load level ranging from 640 to 1,390 kg/yr with volatilization (at an exchange rate of 0.1 m/d) appears to be representative of observed surface sediment data for the open lake waters. Fifty percent response times for PCB following cessation of load and including volatilization varied from less than 5 years to 10-20 years for the other lakes without volatilization. Comparison of these response times to decline of concentrations of PCB in Lake Michigan indicates that at least for that lake volatilization is occurring at an exchange rate of about 0.1 m/d.

Calculations using a solids dependent partition coefficient for PCB indicate that the total and dissolved PCB concentration in the water column and sediment PCB concentration are affected to less than an order of magnitude. Interstitial PCB concentration however increases by about two orders of magnitude over the case with a solids independent partition coefficient. Higher exposure concentrations to benthic organisms may then result with a potential route of PCBs to the top predators in the food chain.

Calibration of the model to data on benzo(a) pyrene confirms that on a lake-wide scale the principal external source in the atmosphere and for the larger lakes such as Michigan the response time of the lake to external loads is about 6-10 years while for Lake Erie response time is about 2 years.

Application of the model to cadmium in the lakes, using a solids dependent partition coefficient indicates that the lakes do not reach equilibrium over a 100 year period. For constant partitioning, cadmium concentrations reach steady state in about 10-25 years. An estimate of the preceding 50 year average cadmium input ranges from 200-600 g Cd/km^2-yr for the upper lakes to 2,000-10,000 g Cd/km^2 for Lake Erie. Calculated high concentrations of cadmium in interstitial water (e.g., 10 μg/l) indicate the importance of measuring interstitial cadmium concentrations.

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ABSTRACT

A physico-chemical model of the fate of toxic substances in the Great Lakes is constructed from ass balance principles and incorporates principal mechanisms of particulate sorption-desorption, sediment-water and atmosphere-water interactions, and chemical and biochemical decay. The steady state mass balance model of the suspended solids in the open lake water yields net solids settling velocities from 0.02 m/d for Saginaw Bay to 1.33 m/d for Lake Ontario. Calibration of the toxic model is through comparison to plutonium-239 data collected in the 1970's using a 23 year time variable calculation. The calibration at a ^{239}Pu partition coefficient of 400,000 l/kg, a particulate settling velocity of 2.5 m/d, associated lake specific net sedimentation and resuspension velocities provided a good calibration to the observed time variable ^{239}Pu behavior. An assumption of zero resuspension of the sediment did not provide a good calibration. The results indicate that, in general, the sediments are interactive with the water column in the Great Lakes through resuspension and horizontal transport. Fifty percent response times of ^{239}Pu following a cessation of load extend beyond 10 years with sediment resuspension.

The calibrated model was applied to polychlorinated biphenyl (PCB) using a high and low estimate of contemporary external load and with and without volatilization. The results of the application indicate that the upper load level (lake range of 400-9500 kg/yr) without volatilization is not representative of the surface sediment data and very limited water column data. The lower load level (lake range 640-1390 kg/yr) with volatilization (at an exchange rate of 0.1 m/d) appears to be more representative of observed surface sediment data for the open lake waters. Calculated water column concentrations for the lower load level with and without volatilization ranged from 0.25 to 0.90 ng/ℓ for open lake waters. Fifty percent response times for PCB following cessation of load and including volatilization varied from less than 5 years to 10-20 years for the other lakes without volatilization. Comparison of these response times to decline of concentrations of PCB in Lake Michigan indicates that at least for that lake volatilization is occurring at an exchange rate of about 0.1 m/d.

Calculations using a solids dependent partition coefficient for PCB indicate that the total and dissolved PCB concentration in the water column and sediment PCB concentration are affected to less than an order of magnitude. Interstitial PCB concentration however increases by about two orders of magnitude over the case with a solids independent partition coefficient. Higher exposure concentrations to benthic organism may then result with a potential route of PCBs to the top predators in the food chain.

Calibration of the model to limited data on benzo(a) pyrene is obtained with a partition coefficient about one order of magnitude higher than published empirical relationships. The model confirms that on a lake-wide scale the principal external source is the atmosphere and for the larger lakes such as Michigan the response time of the lake to external loads is about 6-10 years while for Lake Erie response time is about 2 years.

Application of the model to cadmium in the lakes, using a solids dependent partition coefficient indicates that the lakes do not reach equilibrium over a 100 year period. For constant partitioning, cadmium concentrations reach steady state in about 10-25 years. An estimate of the preceding 50 year average cadmium input ranges from 200-600 gCd/km^2-yr for the upper lakes to 2000-10,000 gCd/km^2-yr for Lake Erie. Calculated high concentrations of cadmium in interstitial water (e.g. 10 μg/ℓ) indicate the importance of measuring interstitial cadmium concentrations.

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SECTION 1

INTRODUCTION

THE PROBLEM

The input of potentially toxic substances to the Great Lakes (Figure 1) has been the subject of considerable interest over a number of years. The problem contexts have included elevated concentrations of mercury in fish in Lake St. Clair and Lake Erie, atmospheric and nuclear power plant input of radionuclides throughout the Lakes, mirex contamination in Lake Ontario and excessively high concentration of polychlorinated biphenyl (PCB) in the lake trout of Lake Michigan. Several reviews of these and other problem areas associated with toxicants are given by Swain (1980), Delfino (1980) and IJC (1978). In recent years, some problems such as DDT and mercury have declined in significance as concentrations in fish species have dropped to acceptable levels (IJC, 1980). Local near-shore problems, (e.g. mercury in the fish of the Ontario shoreline of Lake Superior) continue however to be a problem. Also, other problem areas appear to be emerging (IJC, 1980). Polychlorinated terphenyls (PCT) have been identified in Lake Erie herring gull eggs and trace levels of dioxin were identified in 1978 in fish taken from Lake Ontario and Saginaw Bay. Indeed over 300 organochlorine compounds and metals such as lead, mercury, zinc and cadmium have been identified in the Great Lakes. The fact that a substance has been identified is not however necessarily representative of a toxic substances problem. The number of such different identifications does indicate that the Great Lakes are receiving a spectrum of complex chemical inputs - some of which may pose a problem if inputs of a particular substance were to increase. Figure 2 shows this distinction. A specific concentration of a chemical in water or in the food chain only reflects the fate of the chemical and not the effect. The effect and consequence of a given "hazardous" substance is a topic of a separate evaluation and is not covered here. The general context of this report then is addressing the problem of the fate of chemicals in the Great Lakes with specific reference to the chemicals that are known to be potentially toxic or hazardous.

OBJECTIVES OF RESEARCH

In order to properly assess the fate of a given toxic substance in the Great Lakes, some overall framework must be available that relates external inputs of the chemical to the resulting concentration of the substance in the water column, sediment and food chain. An understanding of the relative contribution to the distribution of a given chemical from atmospheric, direct discharges, and tributary sources is necessary for effective decision making. Accordingly, the objectives of this research are:

1) to develop a modeling framework for toxic substances in the Great Lakes incorporating the principal features of the physical and chemical mechanisms that determine the fate of an externally inputted chemical,

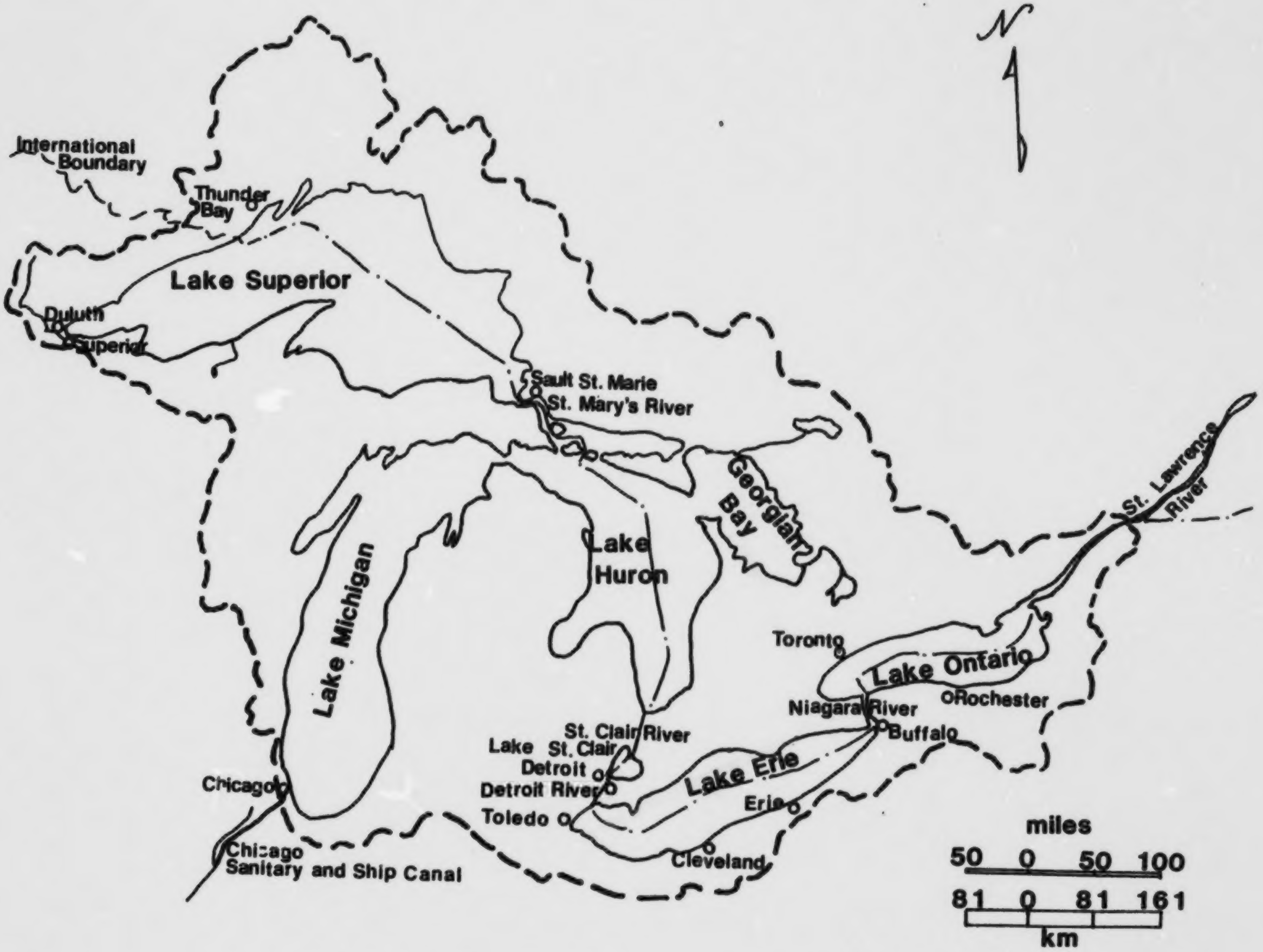

N
International Boundary
Thunder Bay
Lake Superior
Duluth
Superior
Sault St. Marie
St. Mary's River
Georgian Bay
Lake Huron
Lake Michigan
St. Lawrence River
Toronto
Lake Ontario
Rochester
Niagara River
Buffalo
St. Clair River
Lake St. Clair
Detroit
Detroit River
Toledo
Lake Erie
Erie
Cleveland
Chicago
Chicago Sanitary and Ship Canal
miles
50 0 50 100
81 0 81 161
km

Figure 1. The Great Lakes drainage basin

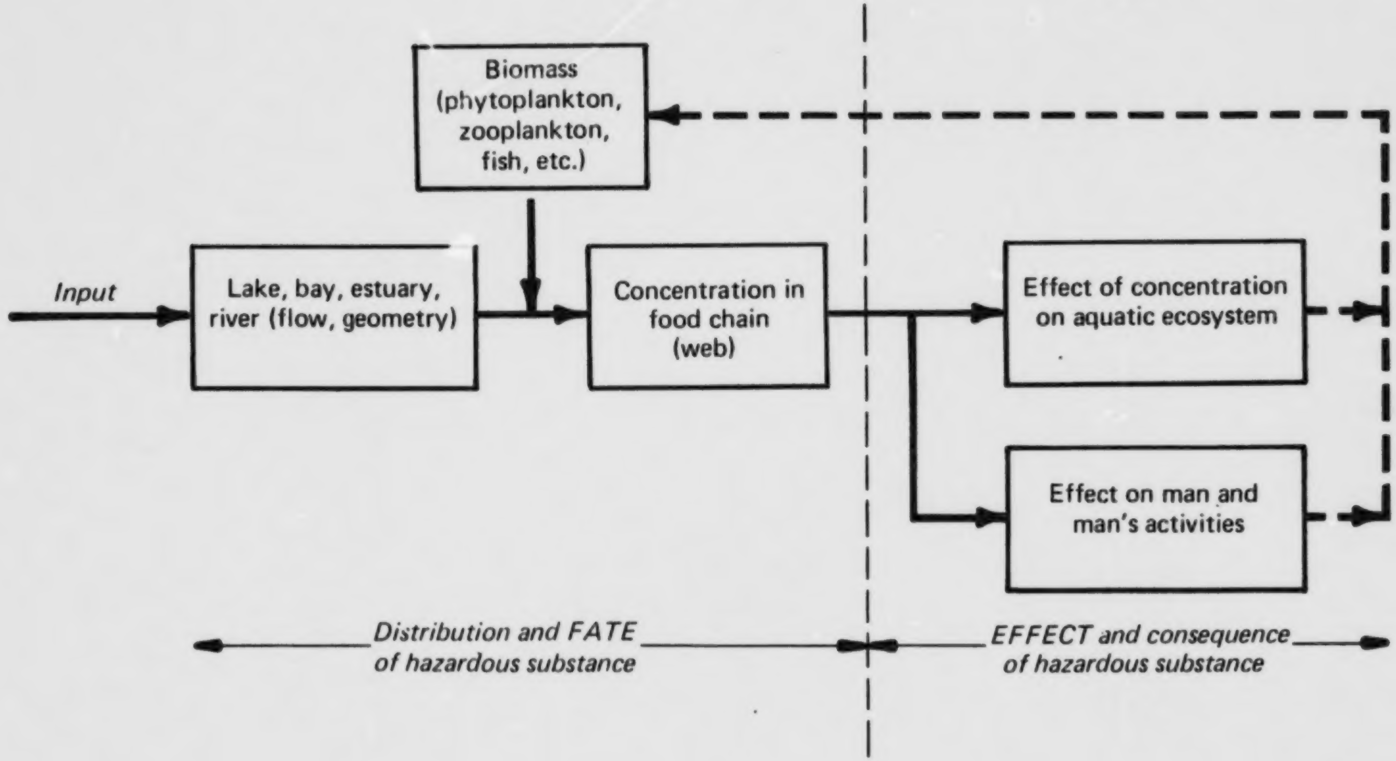

Biomass (phytoplankton, zooplankton, fish, etc.)
Input
Lake, bay, estuary, river (flow, geometry)
Concentration in food chain (web)
Effect of concentration on aquatic ecosystem
Effect on man and man's activities
Distribution and FATE of hazardous substance
EFFECT and consequence of hazardous substance

Figure 2. Distinction between fate and effects of a hazardous substance.

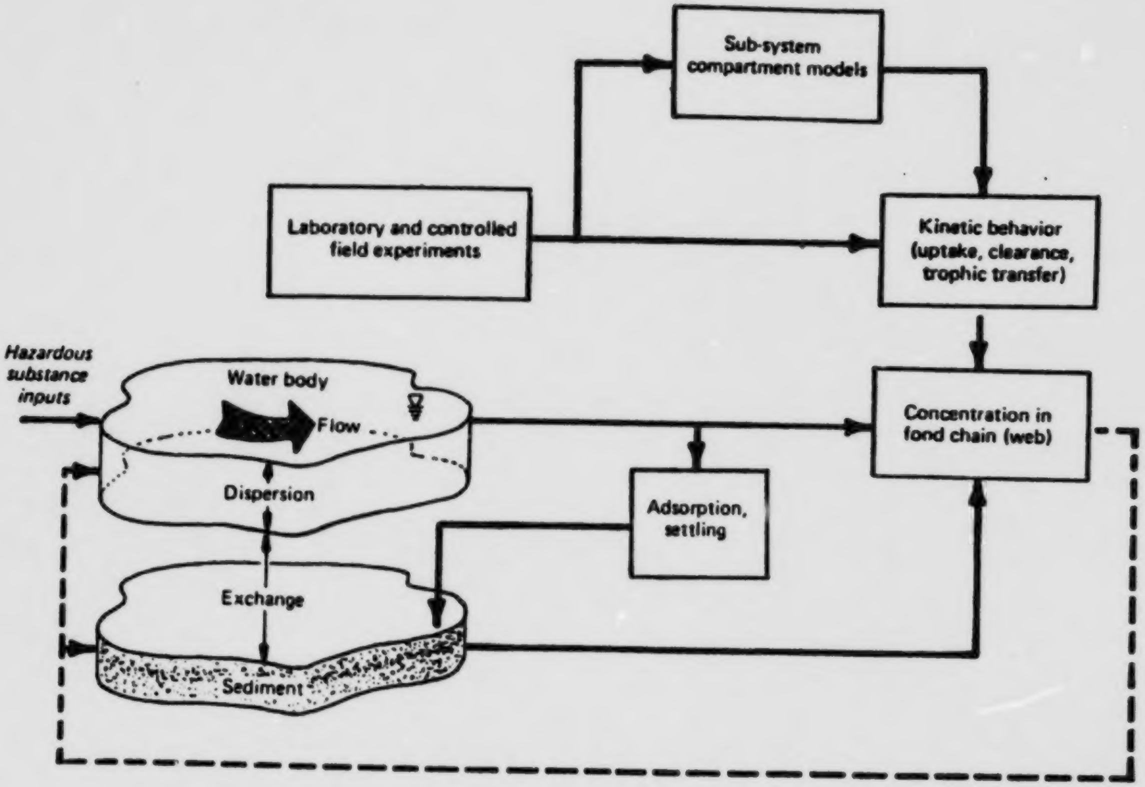

Sub-system compartment models
Laboratory and controlled field experiments
Kinetic behavior (uptake, clearance, trophic transfer)
Hazardous substance inputs
Water body
Flow
Dispersion
Exchange
Sediment
Adsorption, settling
Concentration in fond chain (web)

Figure 3. Principal components of overall modeling framework for fate of toxic chemicals.

2) to calibrate the model using existing data on toxic substances, and

3) to describe, via the modeling framework, the expected response times of the lakes as a whole to reductions in external inputs.

SCOPE OF RESEARCH

Figure 3 shows principal components of the overall framework for assessing the fate of a chemical. Such a framework should include the major features of transport in the water body, particulate sorption, desorption and settling, and sediment exchange. The components of the food chain or food web are of central importance in a credible framework. Finally, the output from laboratory and controlled field experiments are incorporated in sub-system compartment models to assess the kinetic behavior of the given substance in terms of uptake, clearance and trophic level transfers. The estimation of lake response and recovery due to reduction in external chemical inputs therefore involves a complex interaction of field data, laboratory experiments and a theoretical construct that provides the synthesizing framework for making predictions. The model framework is divided into two broad components: the physical-chemical sector and the biological sector.

Mechanistically, this research is confined to development of a toxic fate model for the physical-chemical sector of the environment. The development of a model of the fate of a chemical in the aquatic ecosystem is discussed in Thomann (1981) and Thomann and Connolly, (1983).

Geographically, the scope of the research is on a Great Lake scale. With the exception of Saginaw Bay, the modeling framework is considered as representative of the fate of a chemical in the open lake waters. Localized problem areas in the vicinity of harbors, entering tributaries or direct discharge inputs are therefore not part of the geographical scope. The modeling framework is intended to answer questions related to overall open-lake response to external inputs and the interaction of upstream lakes on downstream lakes and the interaction of a large lake such as Lake Huron on a bay such as Saginaw Bay.

The application of this research is also focused principally on toxic substances that are sorbed to particulates and tend to be persistent and not subject to segnificant losses due to, for example, bacterial degradation. The modeling framework however as derived in Section 4 is general and can address the complete spectrum of toxic substances. Therefore,substances that are readily biodegradable, volatilize easily and are not sorbed significantly into particulates present no new difficulties in the modeling structure. Substances that interact strongly with particulates on the other hand introduce the entire domain of solids transport, settling, resuspension and sedimentation. For this reason, this research is focused principally on persistent hydrophobic toxicants; specifically as noted below plutonium -239 as a calibrating variable and polychlorinated biphenyl (PCB) as a contemporary chemical of specific interest.

SECTION 2

CONCLUSIONS

A physico-chemical model of the fate of toxic substances in the Great Lakes can be constructed from mass balance principles to incorporate principal mechanisms of particulate sorption-desorption, sediment-water and atmosphere-water interactions, and chemical and biochemical decay. Valuable insight into the behavior of the fate of chemicals in the lakes or regions of the lakes can be obtained from both steady state models of water column and sediment interactions and time variable models. For the latter models, and for the open waters of the lakes the relevant time scale for toxic substances fate calculations is in the order of years.

Steady state modeling in general does not require specification of the sediment resuspension effects but requires only estimates of the net exchange (settling-resuspension) between the sediment and water column. A limited comparison to observed metal data for Lake Ontario appears to confirm the general structure of the steady state model. Calibration of a two-dimensional steady state model to the PCBs of Saginaw Bay in 1979 indicates the following:

1) Approximately 30% of the total PCBs entering Saginaw Bay from external loads is incorporated into the sediments of the Bay and approximately 70% is exchanged with Lake Huron.

2) Approximately 25% of the peak concentration in the Bay is due to the boundary condition with Lake Huron and the remaining 75% is the effect of the external loads. Complete removal of the Saginaw River loads and maintenance of the Lake Huron boundary at 10 ng/ℓ would result in at least a 75% reduction in the peak PCB concentration under the new steady-state condition. Additional reduction would occur since some significant fraction of the local Lake Huron boundary concentration is probably caused by the loads to Saginaw Bay.

The time variable model of the physio-chemical behavior of potentially toxic substances discharged into the Great Lakes can be calibrated in an internally consistent manner through use of data on the historical loading and resulting response of plutonium-239. The calibration is internally consistent but not necessarily unique. Other internally consistent sets of parameters are possible given the available data.

The available solids data including solids loading, water column concentrations and sediment porosity and density permit an estimate of the net flux of solids to the sediments but do not permit a separation of settling and suspension effects. The steady state mass balance model of the suspended solids in the open lake water yields net solids settling velocities from 0.02 m/d for Saginaw Bay to 1.22 m/d for Lake Ontario. Further calibration using the tracer plutonium-239 was required to delineate settling and resuspension effects.

The following conclusions may be drawn from the calibration of the model to the $^{239,240}Pu$ data and the associated sensitivity analyses.

(1) Particulate settling velocity of 2.5 m/d to 5 m/d with resulting resuspension velocity to maintain a solids balance is operative throughout the Lakes. The resuspension velocity should be viewed as a parameter of the model representing the complex interaction of near shore resuspension, horizontal transport and deposition and open lake resuspension and transport. Chambers and Eadie (1981) in their work on particulate matter in Lake Michigan report transient resuspension phenomena vertically and horizontally that tend to result in large scale resuspension of particulates.

(2) The result of the inclusion of the resuspension phenomena is to retain concentrations of plutonium in the water column over longer periods of time than would occur without the mechanism. This appears to be consistent with the observed data.

(3) The calibration to the observed sediment data in Lake Michigan indicates that some sediment mixing between the 2 cm layers may be occurring as a result of mechanisms such as bioturbation.

(4) The sensitivity analyses indicate that the dynamic behavior of the water column concentration of plutonium is most sensitive to variations in settling and resuspension velocities, and partition coefficients. The 0-2 cm sediment plutonium concentrations do not vary significantly as a function of settling and resuspension characteristics or partition coefficient indicating that data over the 0-2 cm depth is not a sensitive calibrating data set for use in determining model parameters of settling and resuspension.

(5) The time variable calculations result in system behavior of a chemical such as plutonium that is different than the steady state. For example, the calculations indicate that the particulate plutonium decreases with increasing partition coefficient for certain Lakes (e.g. Western Lake Erie).

It is concluded from the application of the plutonium calibrated model to PCBs in the Great Lakes that:

a) the estimated upper level of present PCB loading (ranging from 4080 kg/yr for Lake Ontario to 9500 kg/yr for Lake Superior) without volatilization is probably too high,

b) from the available data, it is not possible, at the present time, to distinguish the appropriate combination of loading and loss due to volatilization,

c) lower levels of PCB in Lake Erie are probably due to the higher net loss of PCB from elevated solids concentrations and resulting fraction of PCB in the particulate form.

d) the response time for Lake Michigan to equilibrate to a steady PCB load with volatilization is less than 20 years for the water column but greater than 20 years for the sediment.

e) the Western Basin of Lake Erie delivers the highest net flux of PCB to the sediment of the three basins of the Lake.

f) volatilization of PCB is significant for Lake Michigan (about 65% of incoming load) but is less significant for Lake Erie (about 8%) due to the higher solids concentration in that lake.

It is concluded from calculations of response times that for large lakes such as Michigan where response times are relatively long, a water column/sediment equilibrium model is not appropriate since the sediment response time is markedly different than the water column. The inclusion of sediment resuspension and interaction increases the response time of nonreactive but particulate sorptive substance such as plutonium by about an order of magnitude over the case where resuspension is assumed to be zero.

For PCB, the response times due to load reduction of external sources of PCB may vary by an order of magnitude depending on the magnitude of the volatilization of 5-10 years or longer without volatilization. Comparison of these response times to observed declines in concentrations of PCB bloaters indicate that volatilization of PCB is occurring at an exchange rate of about 0.1 m/d at least for that lake.

Model calculations were also perfomed using a solids dependent partition coefficient for plutonium 239 and PCB. For plutonium, the results indicate that particulate settling velocities of 2.5-5.0 m/day, with or without solids dependent partitioning (at a log slope for solids of -.435) and associated sediment diffusion provide an approximately equal representation of the observed data. A more marked solids dependence (log slope of -1) of the partition coefficient did not provide an acceptable comparison to the observed data.

From the calculation on the sensitivity of the PCB distribution in the Great Lakes to a sediment dependent partition coefficient, it is concluded that:

(1) such a relationship is more representative of the observed particulate and sediment PCB data in Lake Michigan;

(2) total and dissolved PCB concentration in the water column and sediment PCB concentration are not affected significantly (i.e. by at least one order of magnitude) under a solids dependent partitioning assumption;

(3) interstitial PCB concentration in the sediment is affected markedly by such an assumption and an increase of about two orders of magnitude is calculated.

(4) since the increased interstitial PCB concentration in the sediment is about two orders of magnitude higher than the overlying water

dissolved PCB concentrations, one would expect benthic organisms to carry a significantly higher body burden than organisms exposed solely to the water column and as a result would be a potential significant source of PCBs to top predators in the food chain.

Additional applications were made to benzo(a) pyrene (BaP) and cadmium for the Great Lakes. For BaP, it is concluded that:

(1) the estimate of the BaP partition coefficient obtained from published empirical relationships is probably low by about an order of magnitude for the Great Lakes system,

(2) with an increased BaP partition coefficient and assuming loss due to volatilization, the physico-chemical toxic substances model of the Great Lakes approximate observed BaP water column and sediment data to order of magnitude,

(3) the model confirms that on a lake-wide scale, the principal external source of BaP is the atmosphere,

(4) for the larger lakes such as Michigan, the 50% response time of the lake to a step increase in external loads is about 6-10 years for the water column - sediment system while for Lake Erie the response time is about two years,

(5) lake to lake variations in calculated BaP water column and sediment concentrations are less than a factor of two.

It is concluded from this application of the physico-chemical model to cadmium in the Great Lakes that

1) The degree of any dependence of the cadmium partition coefficient with solids has a marked effect on time to steady state and interstitial cadmium concentration.
2) Under a solids dependent cadmium partition assumption, the Great Lakes, especially the upper Lakes, do not reach a steady state condition after 100 years of constant loading.
3) Under a constant partition coefficient for cadmium, the Lakes do reach an equilibrium condition varying from about 25 years for Lake Michigan to 10 years for Lake Erie.
4) The concentration of cadmium in the Lakes would be expected to increase by about 60% over the next 50 years if the average cadmium loading for the preceding 50 years continues.
5) Based on assumed sediment cadmium concentrations for Lake Erie, it is estimated that the cadmium concentration in the water column is about an order of magnitude higher than the other Lakes.
6) If loads are projected to increase then cadmium concentrations in the Lake system may increase to levels of concern.

SECTION 3

RECOMMENDATIONS

The following recommendations are offered as a result of this research.

1. The development of the physico-chemical model of the Great Lakes should be continued and additional areas to be explored should include additional calibration analyses, where possible, of PCB isomers and of other chemicals of contemporary interest. Suspended solids data should also be collected from the open waters of the Lakes.

2. Because of the significance of PCBs in the Great Lakes, additional field sampling is necessary for:

a) input load of PCB, e.g. atmospheric, tributary, and point sources,
b) water column PCB concentration, both dissolved and particulate,
c) sediment and interstitial PCB concentration as a function of the depth of sediment,
d) concentration of PCB in the food chain including intermediate organisms (e.g. benthic species, zooplankton, small fish) and top predators (e.g. lake trout).

3. Models of the physico-chemical fate of potential toxic chemicals should be developed for the near-shore and estuarine environment of the lakes with ultimate extension to point sources of chemicals in a given basin. Models on these scales will then provide a basis for assessing the resultant input of chemicals from up-basin discharges on the lake proper and be an important part of an overall waste load chemical allocation scheme.

4. Since there is evidence to indicate a dependence of partition coefficient for PCB and cadmium (among other substances), laboratory work should be conducted over the range of Great Lake solids concentrations to determine the degree of such dependence for representative chemicals.

5. Under assumptions of solids dependent partition coefficient for PCB and cadmium, interstitial water concentrations are calculated at levels several orders of magnitude higher than overlying water concentrations. Field sampling of interstitial water concentrations and benthic organisms of representative substances such as PCB, cadmium and benzo(a) pyrene should be conducted to confirm or deny these estimates.

SECTION 4

MODEL FRAMEWORK
COMPLETE EQUATIONS

The development of a mathematical model for the physical-chemical fate of a toxic substance in water must include the following features:

1. sorption-desorption mechanisms of the chemical with suspended particulates in the water column
2. similar mechanisms with solids in the sediments
3. loss of the chemical due to mechanisms such as biodegradation, volitilization, chemical and biochemical reactions, photolysis
4. transport of the toxicant due to advective flow transport, and dispersion and mixing
5. settling and resuspension mechanisms between sediment and water column
6. direct inclusion of external inputs that may be subject to environmental control.

Figure 4 shows these principal features in a schematic form. The model proceeds from these general features by development of the basic mass balance equations; first for the suspended and sedimented solids in the system and then for the toxicant. For the sake of simplicity in model derivation only a single solids class is considered at this point; i.e., a distinction is not made between sands, silts, or organic particles. The extension to more than one solid class is discussed later.

TOXICANT MASS BALANCE EQUATIONS

The concentration of a toxicant in the water column and in the sediment is given by a mass balance around each of the finite segments of the water body. Referring to Figure 5 and Table 1, Definition of Terms, a mass balance equation can be written around segment 2 as a typical interior segment. The toxicant is composed of two forms: 1) the dissolved form, c'_d, where "dissolved" is considered in an operational manner, i.e. all toxicant passing for example a 0.45 μm filter and 2) the particulate form, c_p, i.e. the toxicant sorbed onto particulate matter in the water column or sediment. As noted above in this derivation, only a single solids class is considered here. The total toxicant concentration is then

$$c_T = c_p + \phi c'_d \qquad (1)$$

$$[M_T/L^3_{s+w}] = [M_T/L^3_{s+w}] + [L^3_w/L^3_{s+w}][M_T/L^3_w]$$

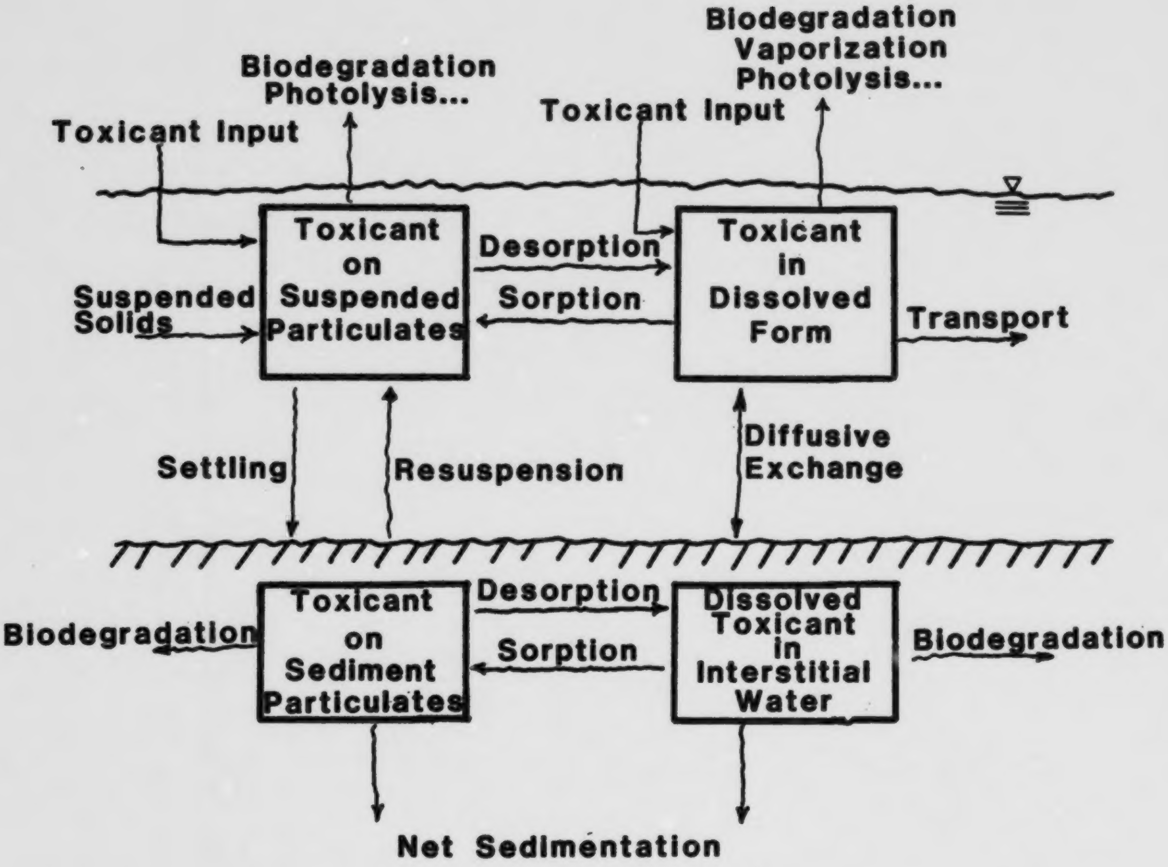

Biodegradation
Photolysis...
Toxicant Input
Biodegradation
Vaporization
Photolysis...
Toxicant Input
Toxicant on Suspended Particulates
Desorption
Sorption
Toxicant in Dissolved Form
Suspended Solids
Transport
Settling
Resuspension
Diffusive Exchange
Toxicant on Sediment Particulates
Desorption
Sorption
Dissolved Toxicant in Interstitial Water
Biodegradation
Biodegradation
Net Sedimentation

Figure 4. General schematic of principal features of physical chemical fate model.

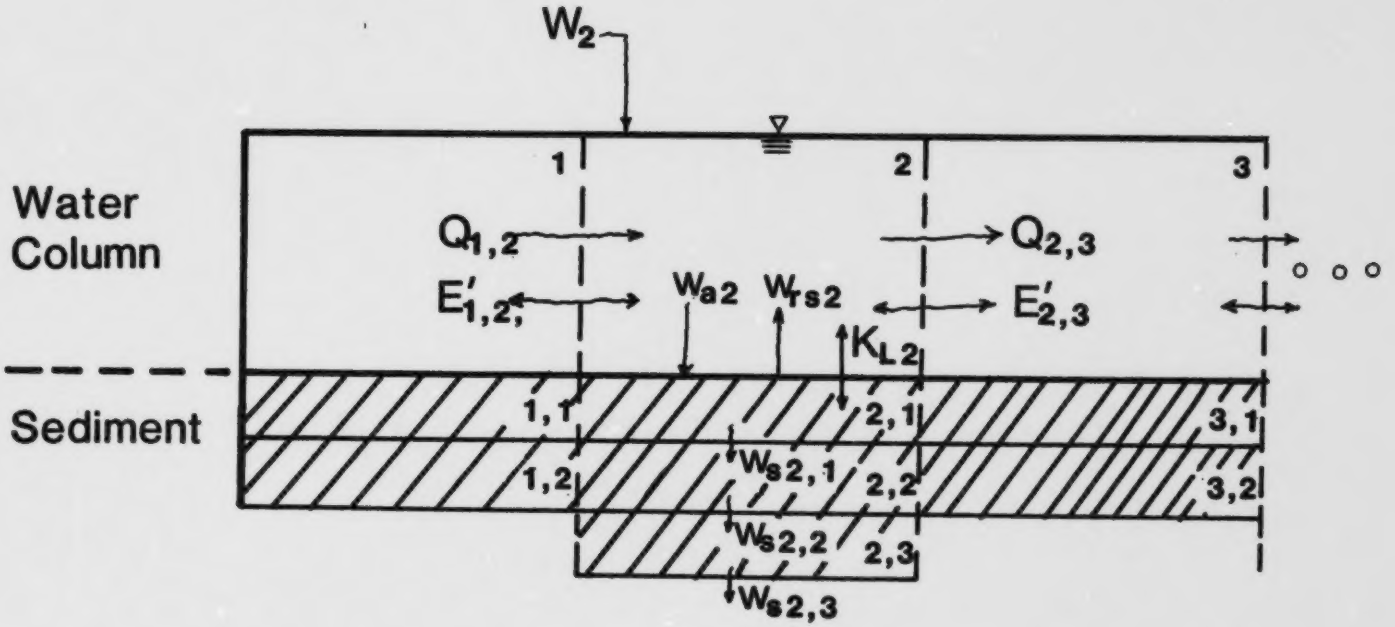

W2
1
2
3
Water Column
Sediment
Q1,2
E'1,2
Q2,3
E'2,3
Wa2
Wrs2
KL2
1,1
1,2
2,1
2,2
2,3
3,1
3,2
Ws2,1
Ws2,2
Ws2,3
o o o

Figure 5. Definition sketch for toxicant mass balance equation.

TABLE 1
DEFINITION OF TERMS

Symbol	Definition	Units[1]
A	Interfacial area	$[L^2]$
c_d	Dissolved toxicant concentration-porosity corrected	$[M_T/L^3_{s+w}]$
c'_d	Dissolved toxicant concentration	$[M_T/L^3_w]$
c_g	Gas phase toxicant concentration	$[M_T/L^3_g]$
c_p	Particulate toxicant concentration	$[M_T/L^3_{s+w}]$
c_T	Total toxicant concentration	$[M_T/L^3 s+w]$
c_w	Solubility of chemical in water	$[M_T/L^3 w]$
E	Dispersion coefficient	$[L^2/T]$
E'	Bulk mixing/dispersion coefficient	$[L^3_{s+w}/T]$
F_s	Net sedimentation flux of solids	$[M_s/L^2\text{-}T]$
f_d	Fraction of toxicant concentration in dissolved form	
f_{oc}	Fraction organic carbon	
f_p	Fraction of toxicant concentration in particulate form	
H	Water column or sediment depth	[L]
H_e	Henry's constant for toxicant	$[M_T/L^3_g\text{-}M_T/L^3_w]$
K	Overall loss rate of total toxicant	[1/T]
K_d	Loss rate of dissolved toxicant	[1/T]
K_g	Gas film rate coefficient for evaporative loss of dissolved toxicant	[L/T]
K_L	Sediment-water diffusive transfer coefficient	[L/T]

TABLE 1 (continued)

Symbol	Definition	Units[1]
K_ℓ	Liquid film rate coefficient for evaporative loss of dissolved toxicant	$[L/T]$
k_u	Sorption (uptake) coefficient	$[L^3_{s+w}/M_s\text{-}T]$
m	Solids concentration	$[M_s/L^3_{s+w}]$
r	Toxicant concentration on solids	$[M_T/L^3 w]$
t_o	Hydraulic detention time	$[T]$
Q	Advective flow transport	$[L^3_{s+w}/T]$
q	Hydraulic overflow rate	$[L/T]$
V	Volume of water column or sediment segment	$[L^3_{s+w}]$
W_a	Surface loading rates of chemical	$[M_T/L^3\text{-}T]$
$W_{m,d,p,T}$	Mass input of solids or dissolved particulate and total toxicant respectively	$[M_T/T]$
W_{ma}	Areal loading of solids	$[M_s/L^2\text{-}T]$
W_{10}	Wind speed 10 m above water surface	$[L/T]$
w_a	Particulate settling velocity	$[L/T]$
w_d	Net dissolved sedimentation velocity	$[L/T]$
w_n	Net loss rate of solids from water column	$[L/T]$
w_{rs}	Particulate resuspension velocity	$[L/T]$
w_s	Net particulate sedimentation velocity	$[L/T]$
w_T	Net removal of toxicant from water column	$[L/T]$
Δx	Characteristic length	$[L]$
$\lambda_{p,g}$	Viscous coefficient for liquid and gas sublayer respectively	
$\nu_{w,a}$	Kinematic viscosity of water and air respectively	$[L\ /T]$
π	Toxicant-solids partition coefficient	$[M_T/M_s \div M_T/L^3 w]$

Symbol	Definition	Units[1]
π'	Toxicant-solids partition coefficient-porosity corrected	$[M_T/M_s \div M_T/L^3_{s+w}]$
π_{ow}	Octanol-water partition coefficient	$[M_T/L^3_o \div M_T/L^3_w]$
π_{oc}	Partition coefficient-organic carbon basis	$[M_T/M_{oc} \div M_T/L^3_w]$
$\rho_{w,a,s}$	Density of water, air or solids respectively	$[M/L^3]$
ϕ	Porosity	$[L^3_w/L^3_{s+w}]$
ϕ_d	Drag coefficient	

---

[1] $[M]$ = Mass

$[M_s]$ = Mass of solids

$[M_T]$ = Mass of toxicant

$[L]$ = Length

$[L^3_{s+w}]$ = Volume of solids and water, i.e. bulk volume

$[L^3_w]$ = Volume of water

$[L^3_g]$ = Volume of gas

$[T]$ = Time

or

$$c_T = c_p + c_d \tag{2}$$

where

$$c_d = \phi c'_d \tag{3}$$

Note that since the dissolved toxicant concentration is the mass of toxicant per volume of water and the total toxicant concentration the mass of toxicant per volume of water plus solids, the porosity of the volume (ϕ) must be introduced to maintain a consistent mass balance. Recognizing the concentration as mass per volume of solids plus water permits a consistent equation set between the water column and the sediment. The quantity, c_d, therefore represents the porosity corrected dissolved form of the toxicant.

Figure 5 is the definition sketch and Table 1 lists the terms, their definition and units. Note that the water column is divided into a series of finite volumes and as shown in Figure 5 are one dimensional, but the configuration of the segmentation can be multidimensional in the water column. The Great Lakes application discussed below is two dimensional (horizontally) in the water column. The water column segments are the primary numbering sequence. The underlying sediment segments are further numbered depending on the overlying water column segment. Thus a variable that is subscripted i, j would be located in the jth sediment layer under the ith water column.

Dissolved toxicant. The mass balance for the dissolved toxicant in the water column segment 2 is given by

$$\begin{aligned}
V_2\frac{dc_{d2}}{dt} = {} & [Q_{12}c_{d1} - Q_{23}c_{d2} + E'_{12}(c_{d1}-c_{d2}) + E'_{23}(c_{d3}-c_{d2})] && \text{(Transport)}\\
& + k_{d2}V_2c_{p2} - k_{u2}m_2V_2c_{d2} && \text{(Sorption-desorption)}\\
& + K_{L2}A_{2,1}(c'_{d2,1} - c'_{d2}) && \text{(Sediment diffusive exchange)}\\
& - K_{d2}V_2c_{d2} && \text{(Decay \& losses)}\\
& - k_{\ell 2}A_2(c_g/H_e - c'_{d2}) && \text{(Volatilization)}\\
& + W_{d2} && \text{(Input)(4)}
\end{aligned}$$

The group of terms in brackets represents the transport and dispersion of the dissolved toxicant. The net transport flows, Q, are written in an equivalent backward difference approximation to the underlying partial differential equation. The dispersion or mixing between segments is given by the bulk dispersion coefficient which in turn is related to the dispersion coefficient by

$$E' = \frac{EA}{\Delta x} \tag{5}$$

The second line on the left of Eq. (4) is the balance between the desorption of the toxicant in the particulate phase ($k_{d2}V_2c_{p2}$) which increases the dissolved form and the adsorption from the dissolved phase onto the particulates given by $k_{u2}M_2V_2c_{d2}$. Note that this latter term depends on the mass of solids available for sorption from the dissolved phase.

The third line of Eq. (4) represents the diffusive exchange between the sediment dissolved toxicant concentration $c_{d2,1}$ in the interstitial water and the dissolved toxicant concentration in the water column, c_{d2}. The sediment-water diffusive transfer coefficient, K_{L2} can be considered as an overall interfacial transfer coefficient relating to the diffusion of the toxicant across the sediment water interface.

Decay and loss mechanisms such as biodegradation, photolysis etc. of the dissolved form are included in the fourth line of the equation. Therefore, K_{d2} represents the sum of individual rates some of which in turn may represent rather complex mechanisms. Note that for this model all the loss rates are assumed to be first order.

Volatilization of the dissolved toxicant is given by the fifth line of Eq. (4). The overall volatilization transfer coefficient is given by (O'Connor, 1982) as

$$\frac{1}{k_\ell} = \frac{1}{K_\ell} + \frac{1}{H_eK_g} \tag{6}$$

Specific formulae for calculating K_ℓ and K_g due to winds for open bodies of water such as the Great Lakes are from O'Connor (1982) as

$$K_\ell = \left[\frac{D_L}{\nu_w}\right]^{2/3} \left[\phi_d \frac{\rho_a}{\rho_w}\right]^{1/2} \frac{W_{10}}{\lambda_\ell} \tag{7}$$

and $$K_g = \left[\frac{D_g}{\nu_a}\right]^{2/3} \left[\phi_d \frac{\rho_a}{\rho_w}\right]^{1/2} \frac{W_{10}}{\lambda_g} \tag{8}$$

The last line represents all external sources or inputs of dissolved toxicant from point direct discharge sources as well as non-point and tributary inputs.

An equation similar to Eq. (4) can be written for the dissolved toxicant in the sediment layer underneath the typical water column segment 2. This layer is designated 2,1. Thus,

$$
\begin{aligned}
V_{2,1}\frac{dc_{d2,1}}{dt} = {} & k_{d2,1} V_{2,1} c_{p2,1} - k_{u2,1} m_{2,1} V_{2,1} c_{d2,1} \\
& + K_{L2} A_{2,1} (c'_{d2} - c'_{d2,1}) \\
& - K_{d2,1} V_{2,1} c_{d2,1} \\
& - w_{d2,1\cdot 2} A_{2,1\cdot 2} c_{d2,1} \\
& + K_{L2,1\cdot 2} A_{2,1\cdot 2} (c'_{d2,2} - c'_{d2,1}) \qquad (9)
\end{aligned}
$$

The first three lines of the left side of Eq. (9) have already been discussed relative to the water column. The fourth line of Eq. (9) expresses the "burial" or transfer down into the sediment of the dissolved toxicant due to net sedimentation or build-up of the sediment layer. Note that the subscript 2, 2.1 refers to the interface between sediment segments #1 and #2 under the second water column segment. The last line of Eq. (9) is the diffusive exchange of dissolved toxicant between the first and second sediment layers under the water column. Similar equations can be written for each successive sediment layer. Note that there are no dissolved transport terms for the sediment thereby indicating that the sediment is assumed to be stationary in the horizontal direction.

Particulate toxicant. The mass balance equation for the toxicant sorbed onto the particulates in the water column segment 2 is given by

$$
\begin{aligned}
V_2\frac{dc_{p2}}{dt} = {} & [Q_{12}c_{p1} - Q_{23}c_{p2} + E'_{12}(c_{p1}-c_{p2}) + E'_{23}(c_{p3}-c_{p2})] && \text{(Transport)} \\
& - k_{d2} V_2 c_{p2} + k_{u2} m_2 V_2 c_{d2} && \text{(Desorption-sorption)} \\
& - w_{a2,1} A_{2,1} c_{p2} && \text{(Particulate settling)} \\
& + w_{rs2,1} A_{2,1} c_{p2,1} && \text{(Particulate resuspension)} \\
& - K_{p2} V_2 c_{p2} && \text{(Decay)} \\
& + W_{p2} && \text{(Input)(10)}
\end{aligned}
$$

The first line of this equation is the transport of the particulate toxicant due to net advection (Q) and dispersion (E'). The particulate toxicant is assumed to be transported in the same manner as the dissolved form. The second line is the sorption-desorption mechanism discussed above and as can be noted for the particulate form, sorption is a source and desorption is a sink of toxicant. The third and fourth lines are respectively the particulate settling of the toxicant from the water column and the resuspension of particulate toxicant from the sediment into the water column. The settling velocity, w_a and the resuspension velocity w_{rs} are functions of particle type (sand, silt, organics) and the hydrodynamics of the water-sediment interface. The fifth line represents any decay mechanisms (e.g. bacterial degradation) of the toxicant on/in the particulates and the last line is the external mass input of particulate toxicant.

The particulate toxicant in the sediment is given by an equation similar to Eq. (10) except that, for this work, the sediment is assumed to be stationary in the horizontal direction. That is, bed load transport or sediment movement horizontally throughout the water body is not considered.

The particulate toxicant equation for the sediment segment underlying segment 2 (i.e. segment 2,1) is then given by

$$\begin{aligned}V_{2,1}\frac{dc_{p2,1}}{dt} = & -k_{d2,1} V_{2,1} c_{p2,1} + k_{u2,1} m_{2,1} V_{2,1} c_{d2,1} \\ & +w_{a2,1} A_{2,1} c_{p2} - w_{rs2,1} A_{2,1} c_{p2,1} \\ & -K_{p2,1} V_{2,1} c_{p2,1} \\ & -w_{s2,1\cdot 2} A_{2,1\cdot 2} c_{p2,1} \\ & +E'_{2,1\cdot 2} (c_{p2,2}-c_{p2,1})\end{aligned} \tag{11}$$

The first three lines of this equation parallel the equivalent mechanisms in the water column (sorption-desorption, settling-resuspension and decay). The fourth line represents the net downward flux of sediment particulate toxicant due to the net sedimentation velocity and the fifth part of the equation is the mixing of the sediment due to factors such as bioturbation or deep sediment mixing. (The dissolved form of the toxicant may also diffuse and exchange downward as noted in Eq. 9). Figure 6 illustrates the net sedimentation velocity and sediment mixing effects. As shown in Fig. 6(a), without sediment mixing, assume a layer of sediment at the surface receives at time t=0 an input of a tracer substance, such as a radionuclide or a pollen pulse or a dye input. At some time Δt later, the surface layer will be buried and will appear at a depth Δz as a well defined plug with no exchange with adjacent sediment segments. From the surface of the sediment then, the layer with the concentration of the tracer substance appears to be moving away at a velocity w_s, the net sedimentation velocity. This velocity is equivalent to the net build-up of the sediment over time. Fig. 6(b) shows a similar effect but including some mixing between the sediment particles or diffusive mixing of the dissolved form. The sediment and diffusive mixing induces some spread and the uniqueness of the tracer layer is not maintained. The downward movement of a toxicant is therefore representative of a classical dispersive-advective transport system in the vertical direction.

LOCAL EQUILIBRIUM EQUATIONS

Eqs. (4) and (9) for the dissolved component and Eqs. (10) and (11) for the particulate component in the water column segments and sediment segments respectively represent the complete set of interactive equations. Note that the coupling of the dissolved and particulate components is through the reaction kinetics of sorption and desorption. Now, for a large number of chemicals, these reaction kinetics tend to be "fast" (i.e. completion times on the order of minutes-hour) compared to the kinetics

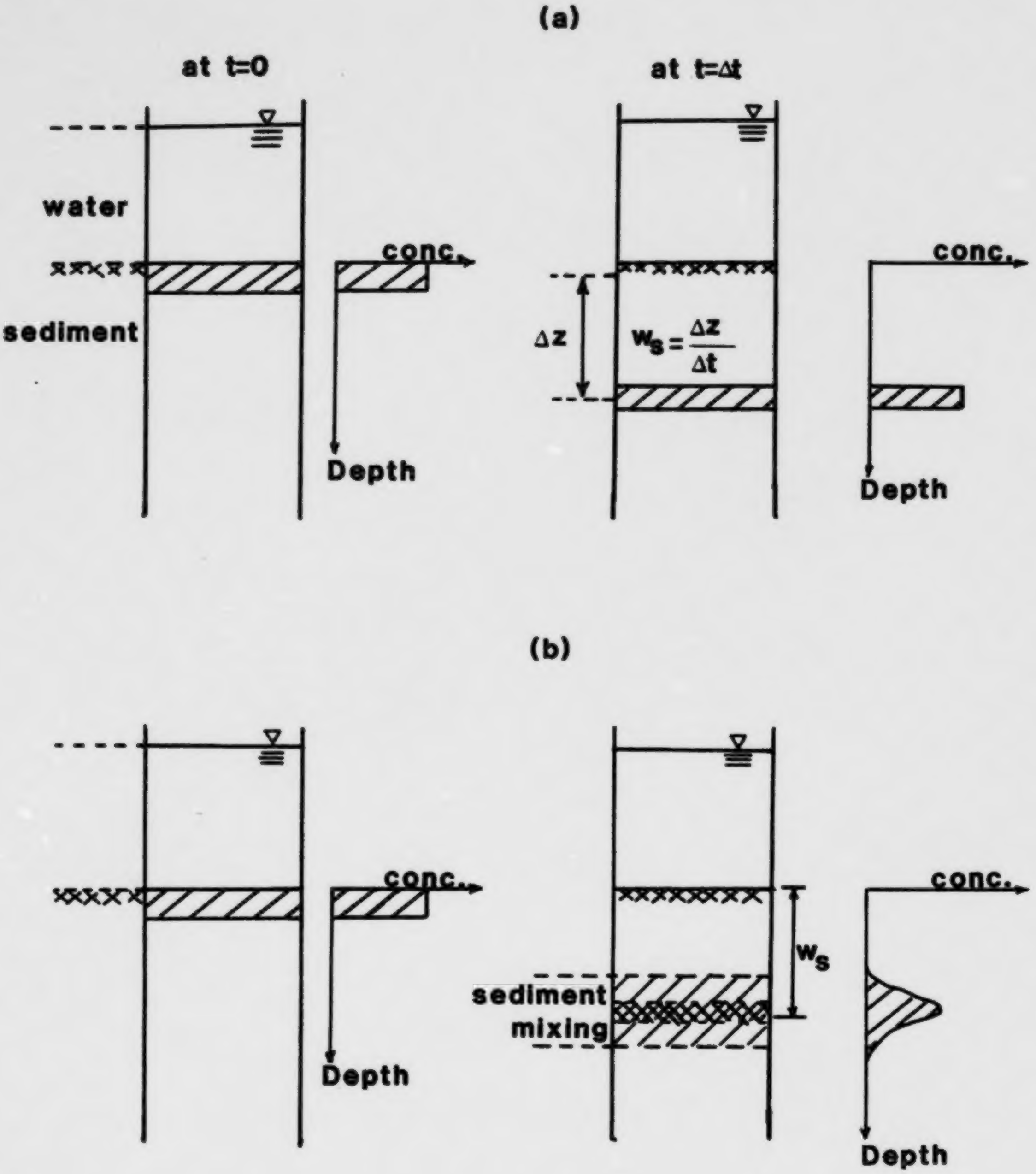

(a)
at t=0
at t=Δt
water
sediment
conc.
Depth
Δz
$w_s = \frac{\Delta z}{\Delta t}$
conc.
Depth
(b)
conc.
Depth
w_s
sediment mixing
conc.
Depth

Figure 6. Illustration of downward advection due to net sedimentation (a) without sediment mixing, (b) with sediment mixing

inherent in other mechanisms of the problem. These latter mechanisms include bacterial decay, net loss rates to the sediment and sedimentation rates that have reaction times on the order of days to years. The equations noted above thus include the entire spectrum of reaction kinetics and as a consequence are quite difficult to solve numerically. Di Toro (1976) has discussed this problem with specific references to water quality models.

The "fast" kinetics of sorption-desorption indicate that for time scales of days to years, there will be a virtually continuous equilibration of the dissolved and particulate forms depending on the local solids concentration. This partitioning between the two components permits the specification of the fraction of dissolved and particulate toxicant to the total. The dissolved and particulate toxicant are therefore assumed to be always in a "local equilibrium" with each other. Assuming that the sorption is reversible (desorption) and that the sorption/desorption kinetics are linear, then a partition coefficient can be defined as follows:

$$\pi = r/c'_d \tag{12}$$

or since $c'_\phi = c_\phi/\phi$

$$\pi' = \pi/\phi = r/c_d \tag{13}$$

Eqs. (12) and (13) describe π as the ratio of the toxicant on the particulate, r, (in units of mass of toxicant per unit mass of dry solids) to the toxicant in the dissolved form.

The particulate toxicant concentration relative to the bulk volume is given by

$$c_p = rm \tag{14}$$

and then the relationship between c_p and c_d is

$$c_p = \pi' m c_d \tag{15}$$

Substituting Eq. (15) into Eq. (2), for the total toxicant gives

$$c_T = (1 + \pi' m) c_d$$

or

$$c_d = f_d c_T \tag{16}$$

where f_d is the fraction of the total that is dissolved and is given by

$$f_d = (1 + \pi' m)^{-1} \tag{17}$$

Recalling that

$$c_d = \phi c'_d$$

then $$c_d = (f_d/\phi)c_T \text{ or } c_d = f_d c_T \text{ for}$$

$$f'_d = f_d/\phi \tag{18}$$

Also, the particulate toxicant as a fraction of total toxicant is given by

$$c_p = f_p c_T \tag{19}$$

for

$$f_p = \frac{\pi' m}{1 + \pi' m} \tag{20}$$

The local equilibrium assumption therefore permits specification at all times and places of the fraction of the total toxicant in the dissolved and particulate form. It should be stressed again here that this local equilibrium assumption assumes complete reversibility between the solid and liquid phases. There is evidence (e.g. DiToro, et al. 1982a) that this is not the case for PCBs. However, this development will proceed on the assumption of reversibility.

Also in these relationships it is assumed that the partition coefficient does not depend on the concentration of the sorbing solids. There is evidence, however, as given by O'Connor and Connolly (1980) that such may not be the case for all chemicals. Di Toro, et al. (1982a) indicate that for PCB the partition coefficient does apparently depend on the concentration of solids. The effect of this dependence with respect to PCBs in the Great Lakes is discussed in Section 10. The development continues here on the assumption of a constant partition coefficient.

Attention can then be focused solely on the mass balance equation for the total toxicant. The total toxicant in the water column or sediment is given by Eq. (2). Adding the water column equations for dissolved toxicant (Eq. 4) and particulate toxicant (Eq. (10)) gives

$$\begin{aligned} V_2 \frac{dc_{T2}}{dt} &= [Q_{12}c_{T1} - Q_{23}c_{T2} + E'_{12}\,(c_{T1} - c_{T2}) + E'_{23}\,(c_{T2} - c_{T2})] \\ &\quad + K_{L2}\,A_{2,1}\,(c'_{d2,1} - c'_{d2}) - K_{d2}V_2c_{d2} + k_{\ell 2}\,A_{2,1}(c_g/H_e - c'_{d2}) \\ &\quad - w_{a2,1}\,A_{2,1}\,c_{p2} + w_{rs2,1}\,A_{2,1}\,c_{p2,1} - K_{p2}\,V_2\,c_{p2} + W_{T2} \end{aligned} \tag{21}$$

Note that the kinetics of sorption-desorption do not appear in this equation because it represents a mass balance of the total. The net loss rates and exchanges that are dependent on the form of the toxicant do however, remain.

Substituting Eqs. (16) and (19) for the dissolved and particulate forms gives an equation entirely in terms of the total toxicant, i.e.

$$
\begin{aligned}
V_2 \frac{dc_{T2}}{dt} = {} & [Q_{12}c_{T1} - Q_{23}c_{T2} + E'_{12}\,(c_{T1}-c_{T2}) + E'_{23}\,(c_{T3}-c_{T2})] \\
& + K_{L2}\,A_{2,1}\,((f'_d\,c_T)_{2,1} - (f'_d c_T)_2) - K_{d2}\,V_2\,(f_d c_T)_2 \\
& + k_{\ell 2}\,A_{2,1}\,(c_g/H_e(f'_d c_T)_2) - w_{a2,1}\,A_{2,1}\,(f_p c_T)_2 \\
& + w_{rs2,1}\,A_{2,1}\,(f_p c_T)_{2,1} - K_{p2}\,V_2\,(f_p c_T)_2 + W_{T2}
\end{aligned}
\tag{22}
$$

This equation represents the mass balance of the total toxicant for the typical water column segment #2. Note that the suspended solids concentration is incorporated in the fraction dissolved and particulate of the total and therefore requires a specification of the concentration or a separate equation for the suspended solids transport.

A total toxicant equation for the sediment segment (number 2,1) underlying segment 2 can be obtained in a similar manner. Thus adding Eqs. (10) and (11) and substituting Eqs. (16) and (19) gives

$$
\begin{aligned}
V_{2,1} \frac{dc_{T2,1}}{dt} = {} & K_{L2}\,A_{2,1}((f'_d c_T)_2 - (f'_d c_T)_{2,1}) - K_{d2,1}V_{2,1}(f_d c_T)_{2,1} \\
& - K_{p2,1}V_{2,1}(f_p c_T)_{2,1} + w_{a2,1}A_{2,1}(f_p c_T)_2 \\
& - w_{rs2,1}\,A_{2,1}\,(f_p c_T)_{2,1} - w_{d2,1\cdot 2}\,A_{2,1\cdot 2}(f'_d c_T)_{2,1} \\
& - w_{s2,1\cdot 2}\,A_{2,1\cdot 2}\,(f_p c_T)_{2,1} + K_{L2,1\cdot 2}\,A_{2,1\cdot 2}((f'_d c_T)_{2,2} \\
& - (f'_d c_T)_{2,1}) + E'_{2,1\cdot 2}\,((f'_p c_T)_{2,2} - (f_p c_T)_{2,1})
\end{aligned}
\tag{23}
$$

Eqs. (22) and (23) are the fundamental total toxicant mass balance equations for a typical water column and underlying sediment segment.

SUSPENDED SOLIDS AND SEDIMENT SOLIDS EQUATIONS

As noted in the above equations, the toxicant equations are coupled parametically to the suspended solids and sediment solids concentrations. The concentrations can be specified externally as input. However, the mechanisms of solids settling and resuspension must therefore be determined by other tracer variables. The solids concentrations can also be computed and calibrated to observed solids concentrations using mass balance equations. The latter course is followed in this work.

Thus for water column segment #2, the solids equation is

$$V_2 \frac{dm_2}{dt} = [Q_{12}\, m_1 - Q_{23}\, m_2 + E'_{12}\, (m_1 - m_2) + E'_{23}\, (m_3 - m_2)]$$
$$- w_{a2,1}\, A_{2,1}\, m_2 + w_{rs2,1}\, A_{2,1}\, m_{2,1} + W_{m2} \qquad (24)$$

Again, the term in brackets is the advective-dispersive transport of the suspended solids. Note that the dispersion is assumed to be the same for the solids as for the toxicant. The settling and resuspension of solids are given by the term involving w_a and w_{rs} and the external input of solids is given by W_{m2}.

For the solids in the sediment segment underlying segment #2 the equation is

$$V_{2,1} \frac{dm_{2,1}}{dt} = w_{a2,1}\, A_{2,1}\, m_2 - w_{rs2,1}\, A_{2,1}\, m_{2,1} - w_{s2,1\cdot 2}\, A_{2,1\cdot 2}\, m_{2,1}$$
$$+ E'_{2,1\cdot 2}\, (m_{2,2} - m_{2,1}) \qquad (25)$$

This sediment solids equation represents a balance between solids settling into the sediment, resuspension from sediment, net sedimentation of solids and solids mixing in the sediment.

Since solids concentrations are given in mass of solids per bulk volume, the concentration is related to the density of the solids and the porosity by

$$m = \rho_s (1 - \phi) \qquad (26)$$
$$[M/L^3_{s+w}] = [M_s/L^3_s][L^3_s/L^3_{s+w}]$$
$$\text{or} \quad m = \rho_s (1 - \phi) \cdot 10^6 \qquad (26a)$$

for ρ_s in g/cm^3 and m in mg/ℓ_{w+s}. Note, therefore, that m is the bulk density of a given volume which has practical significance only in the sediment segments.

TOXICANT EQUATIONS - SEVERAL SOLIDS CLASSES

The equations for the case where there are several solids classes representing for example, fine grain solids and organic particulates such as the phytoplankton are similar to those derived above. The total toxicant is given by

$$c_T = \sum_{k=1}^{m} c_{pk} + c_d \qquad (27)$$

for m size classes. The fraction particulate and fraction dissolved for the kth class are given by

$$f_{pk} = \frac{\pi'_k m_k}{1+\Sigma\pi'_k m_k} \qquad (28)$$

and

$$f_d = \frac{1}{1+\underset{k}{\Sigma}\pi'_k m_k} \qquad (28a)$$

The concentration of particulate toxicant in the kth size class is

$$c_{pk} = f_{pk}c_T \qquad (29)$$

and the dissolved concentration is given as before (Eq. 16). With these expressions, the previously derived toxicant equations for the water column (Eq. 22) and the sediment (Eq. 23) and the solids equations (Eqs. 24 and 25) can be viewed as representing several size classes. The only difference is that all terms involving particulate toxicant must include the sum of the individual size classes. Therefore in Eq. (22), the settling, resuspension, and decay terms for the particulate become

$$V_2 \frac{dc_{T2}}{dt} = \ldots + \sum_{k=1}^{m} \left(-(w_{a2,1})\ A_{2,1}\ (f_{pk}c_T)_2 + (w_{rs2,1})_k\ A_{2,1}(f_{pk}c_T)_{2,1} - (K_{pL})_k\ V_2\ (f_{pk}c_T)_2\right) \qquad (30)$$

Similar extensions can be made for Eq. 23, the toxicant in the sediment layer. For the solids concentrations, a separate equation must now be written for each of the solids class. Equations (24) and (25) are then subscripted for each solids class. The total number of equations for a given segment that must then be solved is equal to the number of solids classes plus one equation for the total toxicant or m + 1.

SECTION 5

SIMPLIFIED MODEL ANALYSES

The preceding development of the complete time variable, multi-solids class and spatially variable equations does not by itself increase understanding of toxicant behavior. This is precisely because of the many complex interactions between the water column and sediment, and the particulate and dissolved toxicant. It is of value then to explore several simplifications of the general equations to further elucidate the role that key mechanisms play in the fate of a specific chemical. Also, simplifications of the general model may prove useful in rapidly assessing and screening potential new chemicals that may enter systems such as the Great Lakes. Finally, simplifications may be possible for certain classes of chemicals that exhibit mechanistic behavior in broadly similar fashions. Two categories of simplification are considered then in this section:

1) Simplification due to chemical behavior

2) Steady state simplification

    a) completely mixed lake
    b) multi-dimensional lake

SIMPLIFICATION DUE TO CHEMICAL BEHAVIOR

The general equations indicate that the characteristics that are chemical specific are

1) Partition of chemical between solids and water

2) Volatilization of chemical across air-water interface

3) Decay of chemical due to photolysis, bacterial degradation, hydrolysis.

The structural properties of chemicals determine the degree to which a given chemical exhibits certain behavior after discharge into a natural body of water. Chemicals will tend to fall into certain groupings reflective of these structural properties nad therefore groups of chemicals can be examined to determine possible simplifications of the preceding equations. Numerous attempts have been made to relate the kinetics of chemicals to specific properties, most notably the octanol/water partition coefficient and the solubility of the chemical in water.

Empirical Relationships of Chemical Kinetics Octanol/water-solubility equations

Chiou et al. (1977) in investigations into the bioconcentration factors for fish suggested the following relationship between the octanol/water partition coefficient and water solubility:

$$\log \pi_{ow} = 5.00 - 0.67 \log c_w \tag{31}$$

$$\text{or} \quad \pi_{ow} = 10^5 c_w^{-.67}$$

where π_{ow} is the octanol-water partition coefficient and c_w, the chemical solubility in water is in μ mol/ℓ. Chiou et al. (1977) indicate that this relationship is valid for estimating π_{ow} to one order of magnitude. This relationship however does not distinguish between liquids and solids. Banerjie et al. (1980) examined this latter distinction and provided the following overall equation

$$\log \pi_{ow} = 5.2 - 0.68 \log c_w \tag{32}$$

which does not differ significantly from Chiou et al. (1977). Inclusion of the melting point by Banerjie et al. (1980) resulted in the following

$$\log \pi_{ow} = 6.5 - 0.89 \log c_w - 0.015\ (mp) \tag{33}$$

for melting point (mp) in °C.

Solids-water partition coefficient equations. Kenaga and Goring (1978) reviewed the literature on equations relating the chemical partitioning into solids and indicated that the range of partition coefficients is significantly reduced when the organic content of the solids is used as the independent variable. They suggest

$$\log \pi_{oc} = 1.377 + 0.544 \log \pi_{ow} \tag{34}$$

Note that the relationship between the toxicant partition coefficient on a solids basis (π) and the partition coefficient on an organic carbon basis (π_{oc}) is

$$\pi_{oc} = \pi / f_{oc} \tag{35}$$

for f_{oc} as the fraction of organic carbon associated with the solids.

Karickhoff et al. (1979) in measurements of hydrophobic chemicals in natural sediments obtained a linear relationship as

$$\pi_{oc} = 0.63\ \pi_{ow} \tag{36}$$

$$\text{or} \quad \pi = 0.63\ f_{oc} \pi_{ow} \tag{37}$$

$$\text{and} \quad \pi = 6.3 \cdot 10^4\ f_{oc} c_w^{-.67} \tag{38}$$

Eq. (34) differs rather considerably from Eq. (36) and reflects the variability to be expected in attempting to estimate partition coefficients for a broad spectrum of solids types. For a whole sediment with varying solids composition,

$$\pi = \sum_i \pi_i f_i \tag{39}$$

for f_i as the fraction of the total mass given by a specific size class. Using the organic carbon partition coefficients,

$$\pi = \sum_i (\pi_{oc} f_{oc} f)_i \tag{40}$$

Karickhoff et al. (1979) thus suggest that from information on organic carbon content, f_{oc}, distribution of various solids classes and octanol/water coefficient, a reasonable (a factor of 2) estimate of sorption partition coefficient can be made. They maintain however that reported values for π_{ow} in the literature may vary by several orders of magnitude due principally to experimental error.

These expressions can be utilized in assessing the relative fractions of particulate toxicant and dissolved toxicant for different sediment solids concentrations, using Eqs. (17) and (20). These latter equations are plotted in Figure 7 for varying levels of solids partition coefficient, π. The solids concentrations are shown for the ranges of 100-1,000,000 mg/ℓ and the range of solids on Great Lakes sediment is shown. As shown, the fraction of toxicant in the particulate phase in the sediment is 99% or larger for all substances with π of 10^2-10^3 ℓ/kg or greater (or conversely water solubilities of less than about 1-10 μ mol/ℓ). Using Eqs. (31) and (36) and an organic carbon content of 2% (f_{oc} = .02), a conversion between π and c_w (μ mol/ℓ) is shown and some representative organic chemicals are indicated. Examination of Eq. (23), the toxicant sediment equation together with Figure 7 shows that there is a broad group of chemicals where the fraction dissolved in the sediment will be less than .01. Hence, dissolved decay terms, exchange of interstitial dissolved chemical concentration and impacts of dissolved toxicant in the sediment on the overlying water column concentration will tend to be small.

It should be noted, however, the the particle concentration dependency of the partition coefficient is ignored in this analysis and it may markedly affect these results. This issue is addressed in more detail subsequently.

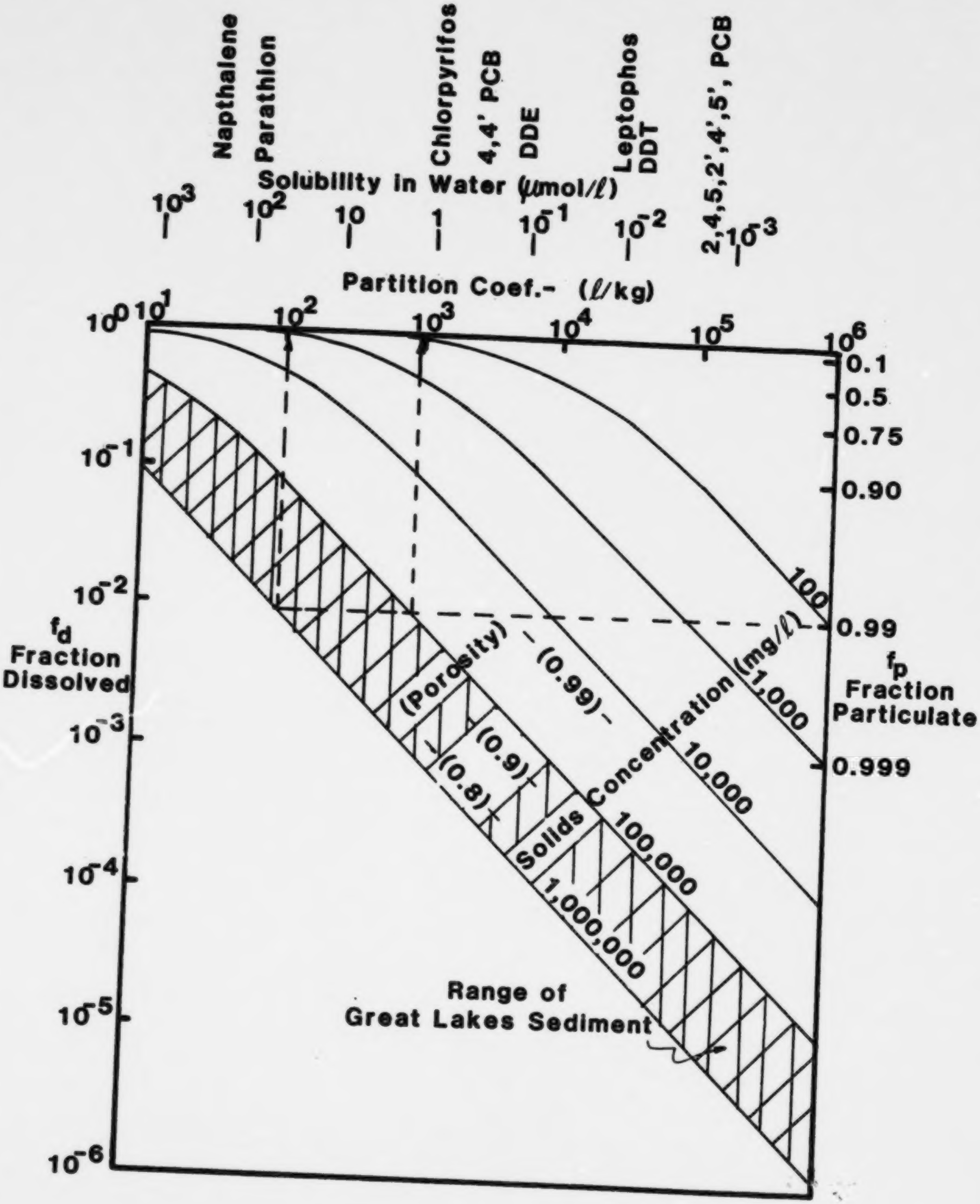


Figure 7. Fraction of particulate and dissolved toxicant for different solids concentrations, partition coefficients and chemical water solubility.

STEADY STATE SIMPLIFICATIONS

Completely Mixed Lake

Considerable insight into the behavior of the general equations can be gained by considering a special case: equilibrium or steady state conditions for a lake that is completely mixed in the water column and interacts with one sediment layer. The steady state assumption does not, of course, permit estimation of how long a sediment would take to depurate when the external load is eliminated. This is a time variable question addressable by the general equations and applied later to the Great Lakes. The steady state assumption is particularly useful for estimating concentrations for chemicals that will continue to be discharged or for screening chemicals to estimate maximum expected concentrations in water column and sediment.

Suspended Solids Model

Since it is known that many chemicals, such as PCBs, sorb to suspended particulate matter, the first step in the development of a simplified model is the mass balance of suspended solids. In this work, a single class of solids is considered and is intended to incorporate inorganic solids and organic particulates.

For a single completely mixed body of water, the mass balance equation for the solids in the water column is given from Eqs. (24) and (25) as:

$$V \frac{dm}{dt} = W_m - Qm - w_a Am + w_{rs} Am_s \tag{41}$$

where as before m and m_s are the concentration of solids in the water column and sediment respectively on a mass per bulk volume basis $[M_s/L^3_{s+w}]$ W_m is the mass input of solids $[M_s/T]$, w_a is the overall lake-wide average particle settling velocity [L/T] of the particulates and w_{rs} is the overall lake-wide resuspension velocity [L/T] of the solids from the sediment to the water column and include parametization of all sediment water particle interactions. Eq. (41) represents a balance of solids between: (a) input of solids externally (W_m) and internally from the flux due to sediment resuspension (w_{rs} A m_s), (b) losses of solids due to flow transport from the lake (Qm) and settling from the water column (w_a A m), and (c) the time rate of change of the solids mass in the water column (V dm/dt). Since Eq. (41) depends on an interaction with the sediment, a similar equation must be written for the sediment segment underlying the water column. Thus following Eq. (25)

$$V_s \frac{dm_s}{dt} = w_a A m - w_{rs} A m_s - w_s A m_s \tag{42}$$

where w_s is the overall lake-wide average net sedimentation velocity of the surface sediment segment [L/T]. The equation for the solids in the sediment then is a flux balance between the incoming solids due to settling from the water column, loss due to resuspension, loss due to net sedimentation ($w_s A m_s$) and the time rate of change of solids in the sediment ($V_s\, d\, m_s/dt$). Note that the sediment is assumed to be stationary and interacting only with the overlying water column. For the Great Lakes model discussed here, the available data on the open lake solids concentration do not permit definition of the time variable behavior of the solids either in the water column or sediment. Although long term secular changes may be occuring in external solids inputs (e.g. from shore line erosion due to variable lake levels), it is not possible to detail such changes nor on the time scale used in this model, does the determination of year to year variation in solids appear necessary. As a result of these considerations, it is assumed that the solids concentrations are at steady state. Therefore, dm/dt and dm_s/dt in Eqs. (41) and (42) are zero. Eq. (42) can then be solved for the sediment concentration and substitution into Eq. (41) yields an equation only in terms of the water column solids concentration, i.e.

$$0 = W_m - Qm - w_n Am \tag{43}$$

where w_n is the net loss of solids from the water column [L/T] and is given by

$$w_n = \frac{w_a w_s}{w_{rs} + w_s} \tag{44}$$

Eq. (43) can be expressed on an areal loading basis as

$$m = \frac{W_{ma}}{q + w_n} \tag{45}$$

where W_{ma} is the areal load [m_s/L^2-T] and q is the ratio of flow to surface area [L/T], the "overflow rate" and is also given by

$$q = H/t_o \tag{46}$$

for depth H[L] and hydraulic detention time t_o [T].

With data on input solids, W_{ma} and observed solids concentration, m, in the water column, Eq. (45) then permits direct estimation of the net loss of solids, w_n. A mass balance around the sediment segment yields (on an areal basis)

$$w_s\, m_s = w_n m \tag{47}$$

which states that the net solids flux into the sediment layer from the water column $[M_s/L^2-T]$ is balanced by the solids flux leaving the sediment segment due to net sedimentation. Note that normal solids budget calculation describe only the balance of the fluxes of solids as in Eq. (43). For a toxic chemical model, however, it is necessary to separate out the solids concentration from the net sedimentation flux. Also, since the solids concentration in the sediment represents the bulk density, the concentration is given by Eq. (26). Then if the density of the solids and the average porosity of the sediment are known, the net effective sedimentation velocity can be estimated from Eqs. (47) and (26) as

$$w_s = \frac{w_n m}{\rho_s (1-\phi)} \tag{48}$$

All of the above relationships apply in principle to a multi-dimensional system where water column segments interact due to advective transport and dispersive mixing as in Eqs. (24) and (25). The equations must then be expanded to include additional terms to reflect the interaction between water segments. Thus, if m_i represents the solids concentration in the i^{th} segment, then at steady state

$$0 = Q_{i-1,i}\, m_{i-1} - Q_{i,i+1} m_i + E'_{i-1,i}\, [m_{i-1} - m_i] + E'_{i,i+1}\, [m_{i+1} - m_i] - w_{ni} m_i + W_{mi} \tag{49}$$

where m_{i-1} and m_{i+1} are the solids concentration in the i-1 and i+1 segments, $[L^3_{s+w}/T]$ and w_{ni} is given again by Eq. (44) for the i^{th} segment.

Toxic Substances Model

Under the steady state assumption, Eqs. (22) and (23) become (where the subscript "s" is the sediment segment, see Figure 8):

$$0 = W_T - Qc_T + K_L A((f_d c_T)_s - f_d c_T) - K_d\, V\, f_d\, c_T + k_\ell A(c_g/H_e - f_d c_T) - w_a A f_p c_T + w_{rs} A\, f_{ps} c_{Ts} - K_p\, V\, f_{ps} c_{Ts} \tag{50}$$

$$0 = - K_L A((f_d c_T)_s - f_d c_T) - (K_d\, V\, f_d c_T)_s - (K_p\, V\, f_p c_T)_s + w_a A\, f_p c_T - w_{rs}\, A\, f_{ps} c_{Ts} - w_d\, A\, f_{ds} c_{Ts} - w_s\, A\, f_{ps} c_{Ts} \tag{51}$$

If the equations are divided by the lake surface area (assumed equal to the sediment-water interfacial area), and terms are grouped, the result is

$$(q + a_{11}) c_T + a_{12}\, c_{Ts} = W_a + k_\ell\, c_g/H_e = W'_a \tag{52a}$$

$$a_{21} c_T + a_{22}\, c_{Ts} = 0 \tag{52b}$$

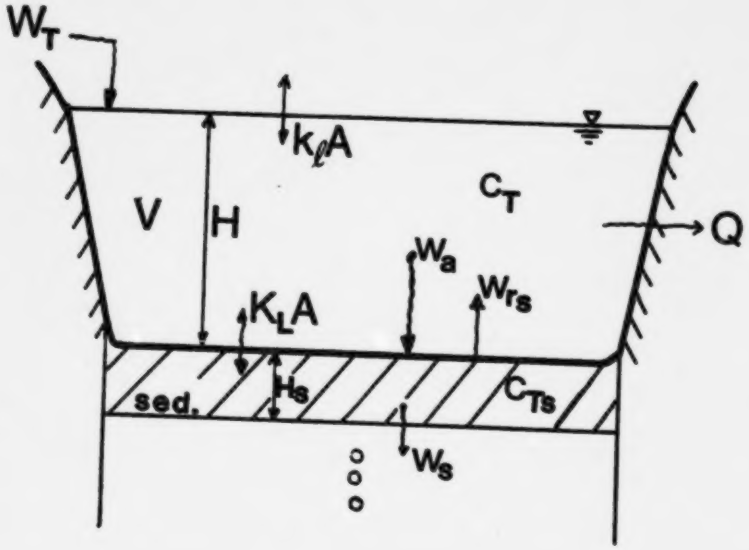

W_T
k_ℓA
V
H
C_T
Q
W_a
W_rs
K_LA
H_s
sed.
C_Ts
W_s

Figure 8. Notation for toxicant distribution in completely mixed lake.

where

$W_a = W_T/A$, the surface loading rate of the chemical

and $a_{11} = (K_L + k_\ell + K_d H) f_d + (w_a + K_p H) f_p$

$a_{12} = - K_L f'_{ds} - w_{rs} f_{ps}$

$a_{21} = - K_L f'_d - w_a f_p$

$a_{22} = (K_L/\phi + w_d + K_{ds} H_s) f_{ds} + (w_{rs} + w_s + K_{ps} H_s) f_{ps}$

Eq. 52b shows that the sediment concentration is a function only of the overlying water column concentration. Therefore, the concentration of the toxicant in the sediment can be solved from Eq. 52b in terms of the concentration in the overlying water as:

$$c_{Ts} = \alpha_T \, c_T \tag{53a}$$

where

$$\alpha_T = \frac{w_a \, f_p + K_L \, f'_d}{(w_{rs} + w_s + K_{ps} H_s) f_{ps} + (w_s + K_L/\phi_s + K_{ds} H_s) f_{ds}} \tag{53b}$$

Substituting Eq. (53a) into Eq. (52a) and simplifying gives

$$0 = W'_a - q c_T - w_T \, c_T \tag{54}$$

where w_T is the net removal rate of the chemical from the water column.

A variety of expressions can be developed for w_T based on the above derivation. A convenient form is given by Di Toro, et al. (1981, 1982b) who have shown that the net loss rate can be expressed as

$$w_T = (K_1 + \beta \frac{r_s}{r} (K_2 + K_s))H \tag{55}$$

where

$$K_1 = (K_d + k_\ell/H) f_d + K_p \, f_p \tag{56}$$

$$K_2 = K_{ds} f_{ds} + K_{ps} f_{ps} \tag{57}$$

$$K_s = \frac{w_s \, f_{ps}}{H_s} \tag{58}$$

and

$$\beta = \frac{m_s \, H_s \, f_p}{m \, H \, f_{ps}} \tag{59}$$

$$\frac{r_s}{r} = \frac{(w_{rs} + w_s)\ f_{ps} + K_L\ (\pi_s/\pi)\ f_{ds}}{(w_{rs} + w_s)\ f_{ps} + K_L f_{ds} + K_2\ H_s} \tag{60}$$

Eq. (54) is informative since it is in a form similar to standard water quality models where all the complex sediment and atmospheric interactions are included in the net removal rate of the toxicant, w_T. This provides for an immediate simplification since now only the water column need be considered. If data are available on the load and resulting water column concentration of a chemical, the net loss rate can be computed from Eq. (54) or if fundamental information is known about the chemical and sediment interactions, w_T can be calculated from Eqs. (55)-(60).

The concentration for the water column is then given from Eq. (54) by

$$c_T = \frac{W'_a}{q + w_T} \tag{61}$$

Figure 9 shows the relationship of Eq. (61) for a range of hydraulic loading rates; net loss rates and resulting ratio of chemical loading to in-lake concentration. For the Figure, w_T is assumed as always negative (sink) although it need not be in general. It can be noted that for hydraulic loading of >100 m/yr., the ratio of the allowable loading to in lake concentration is constant over a wide range of w_T; i.e. the lake hydraulics dominate the kinetics and "flushing" is more important than all of the chemical interactions. For other water bodies, however, such in not the case, although for lakes with lower overflow rates, there is a range over which the allowable loading is independent of w_T.

Eq. (60) shows that if there is no decay of the toxicant in the sediment, and the partition coefficients are equal between the water column and sediment then

$$r_s = r \tag{62}$$

which says that the particulate toxicant concentration in the sediment is equal to the particulate concentration in the water. Also, it can then be shown that for this case

$$w_T = (k_\ell + K_d H) f_d + (w_n + K_p H) f_p \tag{63}$$

This latter result shows that if $r_s = r$, the net loss of chemical from the water column at steady state is readily computed from information on the solids net loss and concentration and properties of the chemical such as decay, volatilization, and solids partitioning. Finally, Eq. (62) indicates that for chemicals that do not appreciably decay or volatilize (as approximated for example by heavy metals and long lived radionuclides),

$$w_T = f_p\ w_n \tag{64}$$

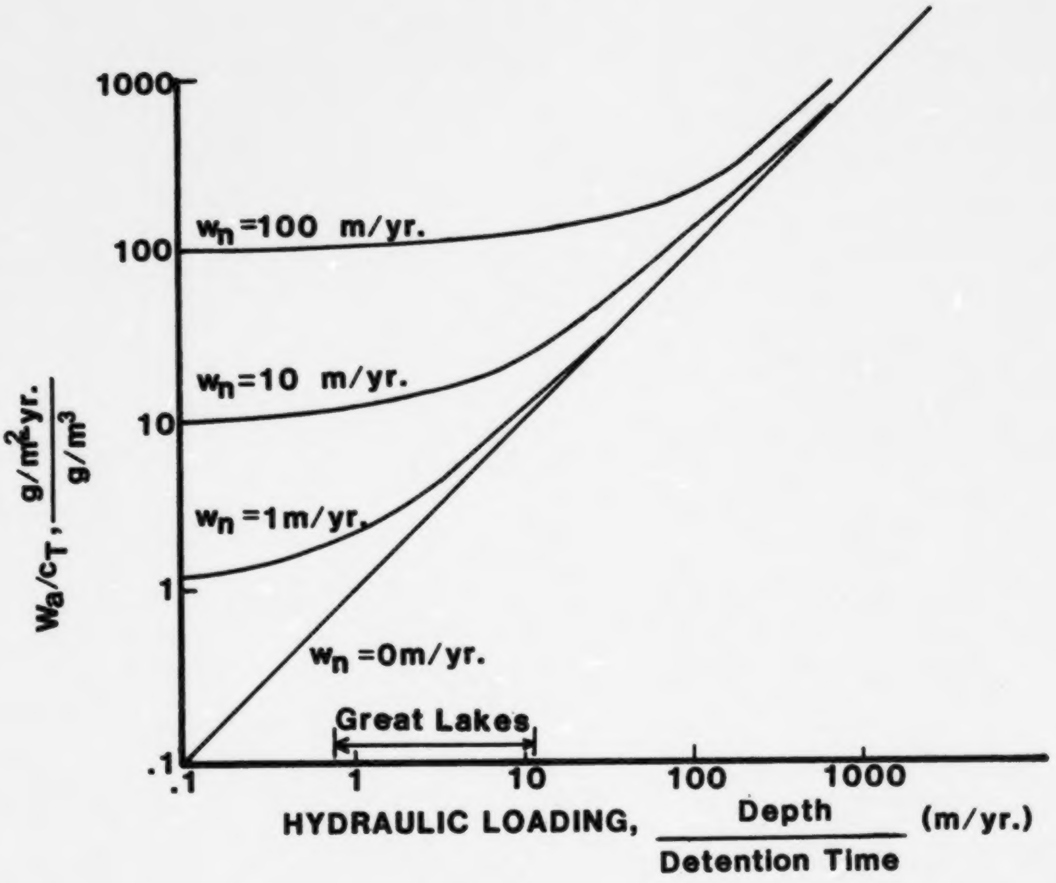


Figure 9. Relationship between hydraulic loading, net loss rate of chemical and chemical loading/in-lake concentration ratio. Net loss always positive(sink)

This result shows that for kinetically conservative chemicals as previously mentioned, the only loss of the chemical from the water column is through the net settling of the fraction of the chemical in the particulate phase.

Figure 10 shows the behavior of the ratio of the net loss of toxicant to solids from Eq. (23) for the case of no volatilization and decay. The heavy metals and long lived radionuclides are examples. The fraction particulate, therefore, is equivalent to the ratio of net toxicant loss to net solids loss. With an estimate of the latter then, the toxicant loss can be estimated.

Also if an estimate is available of the net sedimentation flux rate of solids, $F_s [M/L^2 - T]$, i.e.

$$F_s = w_n m \tag{65}$$

then the net loss of chemical is from Eqs. (64) and (20)

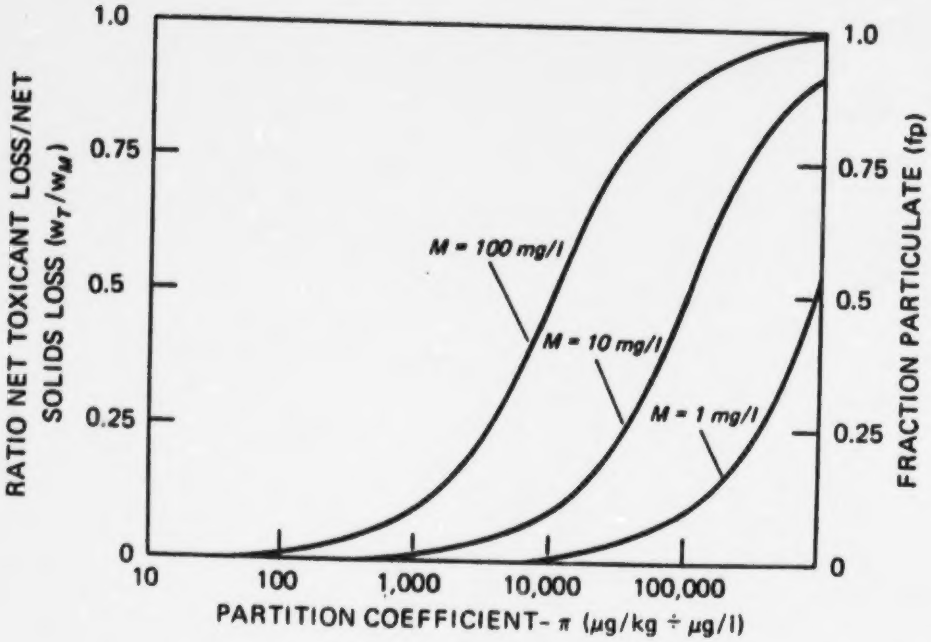
$$w_T = \frac{\pi' F_s}{1 + \pi' m} \tag{66}$$

recognizing that this is for the case of no volatilization or decay. On the other hand, if the chemical loss rate is known from observed data, the equation permits estimate of either the net sedimentation flux, F_s for known solids concentration in the water column, m or estimate of the "effective" steady state solids concentration for known sedimentation flux. Again, all of these relationships are at steady state employ various assumptions and do not apply in general for the time variable situations.

Examples - Steady State

The preceding simplified steady state analyses for the fate of chemicals in lakes indicated that under certain assumptions, the ratio of the concentration of the chemical on the suspended particulate matter is equal to the concentration in the surficial sediments (Eq. 62). Nriagu, et al. (1981) provide data on five metals for Lake Ontario which permit a test of this assumption. The results are shown in Figure 11. In these data, about 20 samples were obtained for the water column and four for the sediment. As shown, for the five metals, the assumption that the particulate concentrations in the water column and sediment are equal is reasonably good. Cadmium is low however by about a factor of two and nickel is high by about a factor of two. To within an order of magnitude, however, these metals appear to behave in accord with the simplified theory.

Table 2 shows the results of the application to two different chemicals in different lakes. The first application, 1,4 dichlorobenzene in Lake Zurich draws on the input data given by Schwarzenbach, et al. (1979). This substance has a low partition coefficient to solids (estimated at 70 μg/kg ÷ μg/ℓ) and, hence, the fraction particulate (for a solids con-



10. Ratio of net chemical loss to solids loass as function of suspended solids concentration and partition coefficient. Dissolved loss = 0.

TABLE 2

TWO APPLICATIONS OF SIMPLIFIED CHEMICAL MODEL

Lake	q (m/yr)	Chemical	π (μg/kg÷μg/ℓ)	Loading g/m^2-yr	Part Chem. Loss (m/yr)[1]	Diss. Chem. Loss (m/yr)[2]	Calc. Conc. (ng/ℓ)	Obs. Conc. (ng/ℓ)
Zurich[3]	40	1,4 dichlorobenzene	70	$1\cdot3\cdot10^{-3}$	0	106	8.9	10
Michigan[4]	0.8	Cadmium	200,000[5]	$0.58\cdot10^{-3}$	12.4	0	43.7	20[6]

1 Calculated from $(\pi M/(1+\pi M))w_n$

2 Calculated from $(1/(1+\pi M))K_1$

3 Input data from Schwarzenbach, et al. (1979)

4 Input data from Muhlbaier & Tisue (1981)

5 From Nriagu, et al. (1981)

6 Lake may not be in equilibrium with load (See Muhlbaier & Tisue (1981))

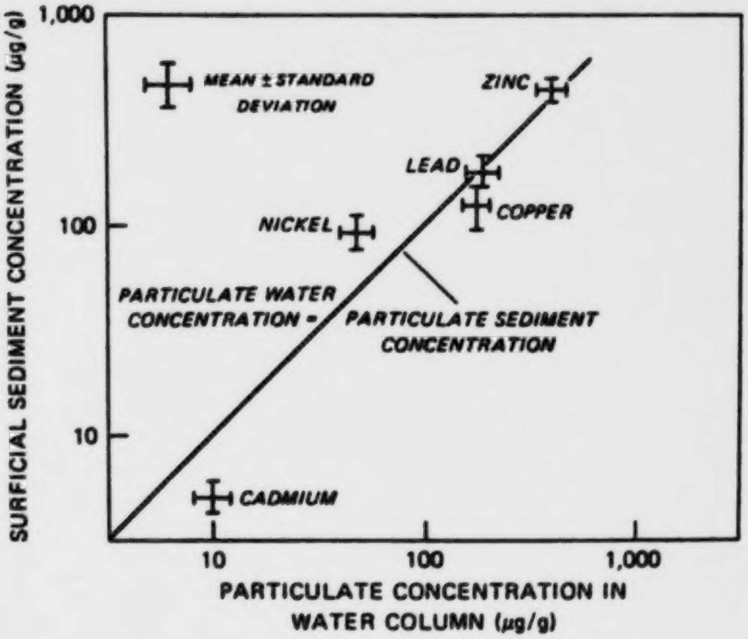
centration of 4 mg/ℓ, (Kelts and Hsii, 1978) is approximately zero. The net loss of the chemical then as shown in Eq. 63 does not depend on settling of the chemical out of the water column but only on the loss of the dissolved fraction. Following the work of O'Connor (1982) using a 5 m/sec. wind, a molecular weight for DCB of 200 and a Henry's constant of 0.2 (Schwarzenbach, et al., 1979), a volatilization exchange rate of 0.29 m/d is calculated (compared to 0.24 calculated by Schwarzenbach, et al. 1979 from a mass balance). The net loss rate for DCB for Lake Zurich is thus about 106 m/yr., all from the dissolved form. Eq. 61 then allows computation of the in-lake concentration of 8.9 ng/ℓ compared to the approximate 10 ng DCB/ℓ observed for Lake Zurich.

The second application was the metal cadmium, which can be highly adsorbed to particulate matter in contrast to DCB. Laboratory data on the partitioning of cadmium indicate a coefficient of about 1000 µg/kg ÷ µg/ℓ (O'Connor and Connolly, 1980) but Nriagu et al. (1981) obtained data on Lake Ontario cadmium that permit an estimation of the partition coefficient of about 200,000 µg/kg÷µg/ℓ. The latter value was used in the calculation shown in Table 2. Muhlbaier and Tisue (1981) provide estimates of loading to southern Lake Michigan which were applied on an areal basis over the entire lake. Net losses of solids for Lake Michigan is estimated at about 137 m/yr. (as discussed later). For 0.5 mg/ℓ suspended solids and a partition coefficient of 200 µg/g÷µg/ℓ, the fraction particulate, f_p is equal to 0.09. If no other loss of cadmium is assumed then the net loss of cadmium is from settling only and is about 12.4 m/yr. Since the outflow loss from Lake Michigan is small (q=0.8 m/yr.), the loss of cadmium is dominated by the sedimentation of particulate cadmium. The calculated in-lake concentration (from Eq. 61) as shown in Table 2 is 44 ng/ or about two times higher than the 20 ng/ℓ considered as observed by Muhlbaier and Tisue (1981). They discuss, at some length, the hypothesis that Lake Michigan because of its long detention time is not in equilibrium with the assumed cadmium load. The simplified steady state model, therefore, approximates the observed cadmium concentration only to order of magnitude (i.e to tens of ng/ℓ) and more reliable data on input and water column, together with a time variable analysis, would be necessary to determine the degree of nonequilibrium for cadmium in Lake Michigan.

Multi-Dimensional Lake

When significant gradients exist in the particular lake or region of lake under study then the completely mixed assumption does not hold. The flux between various regions due to net transport and mixing must be included in the overall steady state simplification. The previous principles for the completely mixed case will be seen to apply in general to the non-homogeneous lake.

Consider then a steady state condition for Eqs. (22) and (23), i.e.



11. Lake Ontario correlation of particulate metals concentration on suspended solids in water column and particulate metals concentration in surficial sediments (calculated from data in Nriagu, et al., 1981).

$$\frac{d\,c_{T2}}{dt} = \frac{d\,c_{T2,1}}{dt} = 0$$

and assume no interaction with the deeper sediment, i.e. consider a single sediment layer with a net downward advection. The result upon adding the two equations is

$$\begin{aligned} 0 = W_{T2} + k_{\ell 2}A_2c_g\ H_e &+ [Q_{12}c_{T1} - Q_{23}c_{T2} + E'_{12}\ (c_{T1}-c_{T2}) + E'_{23}(c_{T3}-c_{T2})] \\ &- [K_{d2}V_2 + k_{\ell 2}A_2)f_{d2} + K_{p2}f_{p2}V_2]c_{T2} \\ &- [(K_{d2,1}V_{2,1} + w_{d2,1.2}A_{2,1})f_{d2,1} \\ &+ (w_{s2,1.2}A_{2,1} + K_{p2,1}\ V_{2,1})f_{p2,1}]c_{T2,1} \end{aligned} \qquad (67)$$

It can be noted that all the interaction terms between the sediment and the water column are eliminated. This is a result of taking the mass balance around the water column and sediment so that the only loss terms are those that are net from the entire system. These net losses are fluxes out due to transport and dispersion, decay in the water column and sediment and net sedimentation of mass out of the sediment segment. Of course, Eq. (67) still includes the sediment total toxicant concentration. Therefore let

$$\alpha_{T2} = \frac{c_{T2,1}}{c_{T2}} = \Pi\,\frac{m_{2,1}}{f_{p2,1}} = [\frac{m_{\ 2,1}}{m_2}\,\frac{f_{p2}}{f_{p2,1}}]\,\frac{r_{2,1}}{r_2} \qquad (68)$$

where

$$\Pi = \frac{r_{2,1}}{c_{T2,1}} \qquad (69)$$

The quantity α is related to the ratio of the chemical concentration in the solids in the sediment and water column and the quantity Π is the ratio of the sediment chemical concentration to the total water concentration, a quantity that is sometimes available from data. Note also from the solids balance (Eq. (44) that

$$\alpha_{T2} = (\frac{w_{n2}}{w_{s2,1.2}})\ (\frac{f_{p2}}{f_{p2,1}})\ \frac{r_{2,1}}{r_2} \qquad (70)$$

Substituting Eq. (68) into (67) and simplifying gives

$$\begin{aligned} 0 = W_{T2} + k_{\ell 2}A_2c_g/H_e &+ [Q_{12}c_{T1}-Q_{23}c_{T2}+E'_{12}(c_{T1}-c_{T2}) + E'_{23}(c_{T3}-c_{T2})] \\ - w_{T2}A_2c_{T2} & \end{aligned} \qquad (71)$$

where w_{T2} is the net loss of toxicant from the water column for segment #2 and is given by Eqs. (55) to (60) with parameters particular to segment #2. Since the net loss rate is segment specific with respect to the water column in a multi-dimensional system, calibration to observed data permits in principle estimates of the net loss of chemical from the water column. Such a net loss includes all interactions with the sediment and atmosphere. Therefore, even for multi-dimensional systems (with a stationary sediment), the net loss rate of the chemical from the water column can be calculated directly from laboratory data on decay and net solids loss rates from Eqs.(55) to (60). This completes the theoretical development of the basic equations and simplifications. Application can now be made to the Great Lakes system including first an application on a steady state basis to solids and PCB in Saginaw Bay and then an analysis of the solids balance and time variable calibration to the radionuclide, plutonium-239,240 on a Great Lakes scale. An application then is made to the PCB distribution also on a Great Lakes scale and the behavior of the response using a solids dependent PCB partition coefficient is explored. Finally, applications of the model are made to benzo(a) pyrene and cadmium.

SECTION 6

STEADY STATE MODEL OF PCBs IN SAGINAW BAY

Saginaw Bay affords an opportunity to test the simple steady state model for PCBs. Richardson, et al. (1983) have summarized the basic data base for Saginaw Bay and the overall properties of the Bay. This application uses the steady-state model previously discussed that incorporates horizontal transport, net solids settling and resuspension and sedimentation, and the interaction of the solids with PCBs.

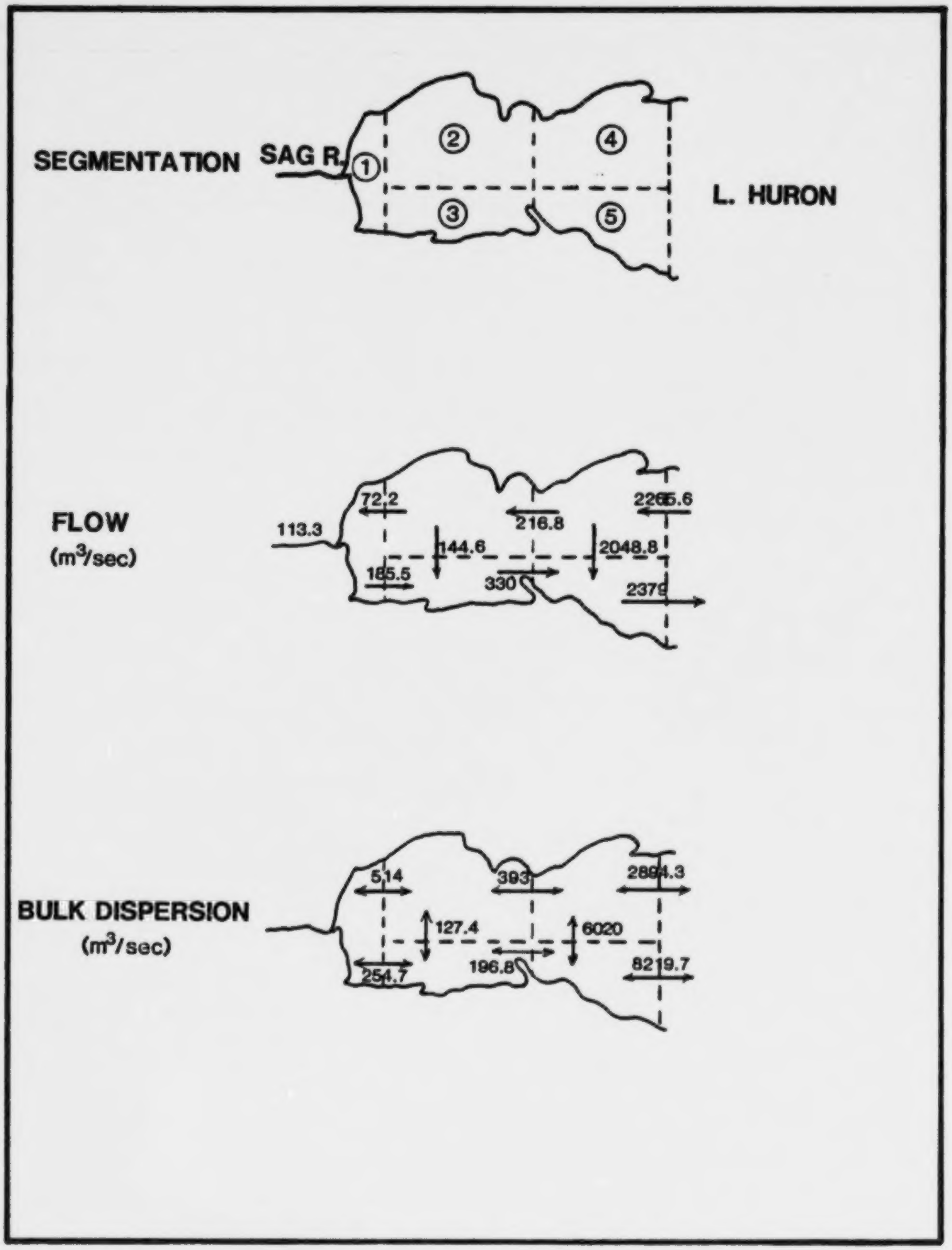
SEGMENTATION & TRANSPORT

The segmentation is from Richardson, et al., (1983) and includes segment volumes, areas, and depths. The dispersive exchange coefficients and the flows between each of the segments and Lake Huron were also obtained from hydrodynamic modeling conducted by the Grosse Ile Laboratory. That work, however, concentrated on the time variable aspects of 1977 and 1979 and, as a result, the coefficients of turbulent exchange and flow have to be modified to represent a long-term steady-state condition. The temporally averaged flows and exchange coefficients that were used in the steady-state computation for the five segments in the water column are as shown in Figure 12 together with the segmentation.

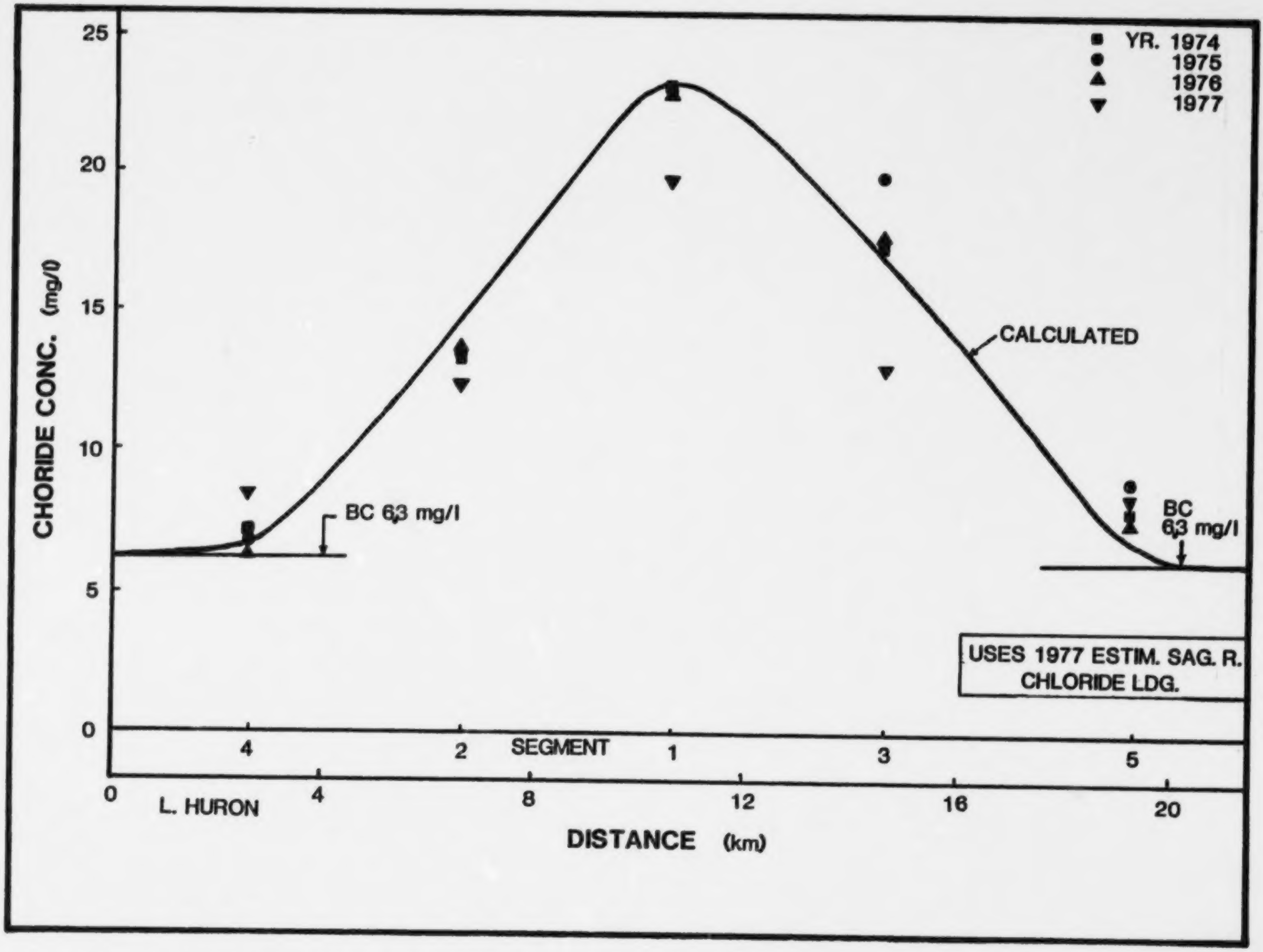
A chloride calibration was then performed using these flows and bulk dispersion values. Chloride data were obtained from STORET for the years 1974 through 1977 and all data found in a segment were averaged for each annual period for that segment. Loadings consisted of the Saginaw River discharge and atmospheric sources (6670 kg/day). Saginaw River chloride loadings for 1974 were estimated to be from 1.04 to 1.15 million kg/day and the 1977 discharge was 0.8 million kg/day. For the calibration, the 1977 value was used. Boundary conditions were selected to be 6.3 mg/ℓ for both segment 4 and 5 on the basis of available STORET data nearest the open lake boundary of the model. The comparison of calculated concentrations of chlorides with the 1974-1977 data in Figure 13 indicates good agreement and, therefore, confirms the transport and dispersion regime as representative of steady state conditions.

SUSPENDED SOLIDS CALIBRATION

The Saginaw River and smaller tributaries to the Bay, shoreline erosion, atmospheric fallout and phytoplankton biomass are the components of solids loads used to calibrate the solids in Saginaw Bay. U.S. EPA (1982) provided a long-term estimate of the Saginaw River load, whereas the contributions of other tributary drainage areas were estimated from average flows and a long-term average suspended solids concentration estimated for the Saginaw River. Bank erosion values were derived from county by county erosion volumes in Monteith and Sonzogni (1976) and proportioned to Saginaw Bay on the basis of shoreline length. Volumes of eroded material were converted to mass loadings by assuming a porosity of approximately 60% and a specific gravity of 2.65. To account for immediate settling of heavier fractions, a 50% reduction was


SEGMENTATION
SAG R.
①
②
③
④
⑤
L. HURON
FLOW
(m³/sec)
113.3
72.2
216.8
2265.6
144.6
2048.8
185.5
330
2379
BULK DISPERSION
(m³/sec)
514
393
2894.3
127.4
6020
254.7
196.8
8219.7

12. Segmentation for Saginaw Bay and estimated long-term average transport coefficients



13. Transport calibration for Saginaw Bay using long-term averaged chloride data.

used to obtain the final estimates. Phytoplankton biomass was obtained from algal model simulations. A summary of all segment loads by class is contained in Table 3. The predominance of the Saginaw River and phytoplankton loadings is apparent.

Boundary conditions, consistent with limited available data, were selected primarily on the basis of trial and error. Preliminary computations indicated that initial estimates of approximately 2 mg/ℓ solids at the open lake boundary were too low since calculated solids concentration in segments 4 and 5 were well below observed values and mass balances of these segments indicated that the boundary fluxes dominated these segments. Final values of 4.3 mg/ℓ for segment 4 and 5.5 mg/ℓ for segment 5 were selected. The former value is thought to be more associated with advective flow entering the Bay from Lake Huron and the latter value more representative of observed segment 5 concentrations leaving the Bay with the net advective flow (see net circulation, Figure 12).

Net removal rates of the suspended solids were then assigned to segments 2,4, and 5 where solids deposition zones are either documented to occur (segment 2) or estimated to occur (segments 4 and 5). No net removal rates were assigned to segments 1 and 3 since sedimentation appeared to be minimal there on the basis of sediment solids and PCB data in sediment cores. Initial values of the net removal rates were made from mass balances of each segment using observed water column solids concentrations. These were then input to the 5 segment Saginaw Bay model, using the transport coefficients previously calibrated, and adjusted until the calculated and observed suspended solids concentrations were in agreement. As seen in Figure 14, the calculated values in the water column are in good agreement with the observed data of 1976 through 1979, when values of the net removal rate of 12.7, 13.8, and 9.7 meters/year are used for segments 2,4, and 5 respectively. Sensitivity analyses indicate that the differences in the net loss rates in segments 2,4, and 5 are not significant. Equally acceptable calibrations are obtained for values between 10 and 20 m/yr. for segments 2, 4, and 5.

With the estimated net removal rate of solids w_n from the water column, the flux of solids into the bed is calculated as $w_{ni}Am_i[m_s/T]$. This is equal to the sedimentation flux which is calculated as $w_{si}Am_{is}$. Since both w_{si} and m_{is} vary with sediment depth, no single value can be specified. However, from Eq. (47) the relationship between w_{si} and m_{is} is unique. If w_{si} is selected, then m_{is} is determined. Log-log plots of the relationships between the sedimentation rate and the bed solids concentration are included in the bottom of Figure 14.

A considerable amount of effort was expended in determining the sediment concentrations of solids (i.e. the bulk density of the sediment) drawing on the work of Robbins (1980). From sediment cores

TABLE 3

ESTIMATED LONG-TERM AVERAGE SUSPENDED SOLIDS INPUTS - SAGINAW BAY

Model Segment	Tributary Loads (lb/day)	Bank Erosion (lb/day)	Atmospheric Loads (lb/day)	Phytoplankton Mass (lb/day)	Total Loading (lb/day)
1	1,232,000*	28,200	10,100	132,200	1,402,500
2	123,900	92,600	31,400	341,600	589,500
3	34,900	63,900	15,100	143,300	257,200
4	21,900	124,100	23,700	176,300	346,000
5	43,700	50,700	24,700	251,300	370,400
Total	1,456,400	359,500	105,000	1,044,700	2,965,600

* Saginaw River 1,208,000

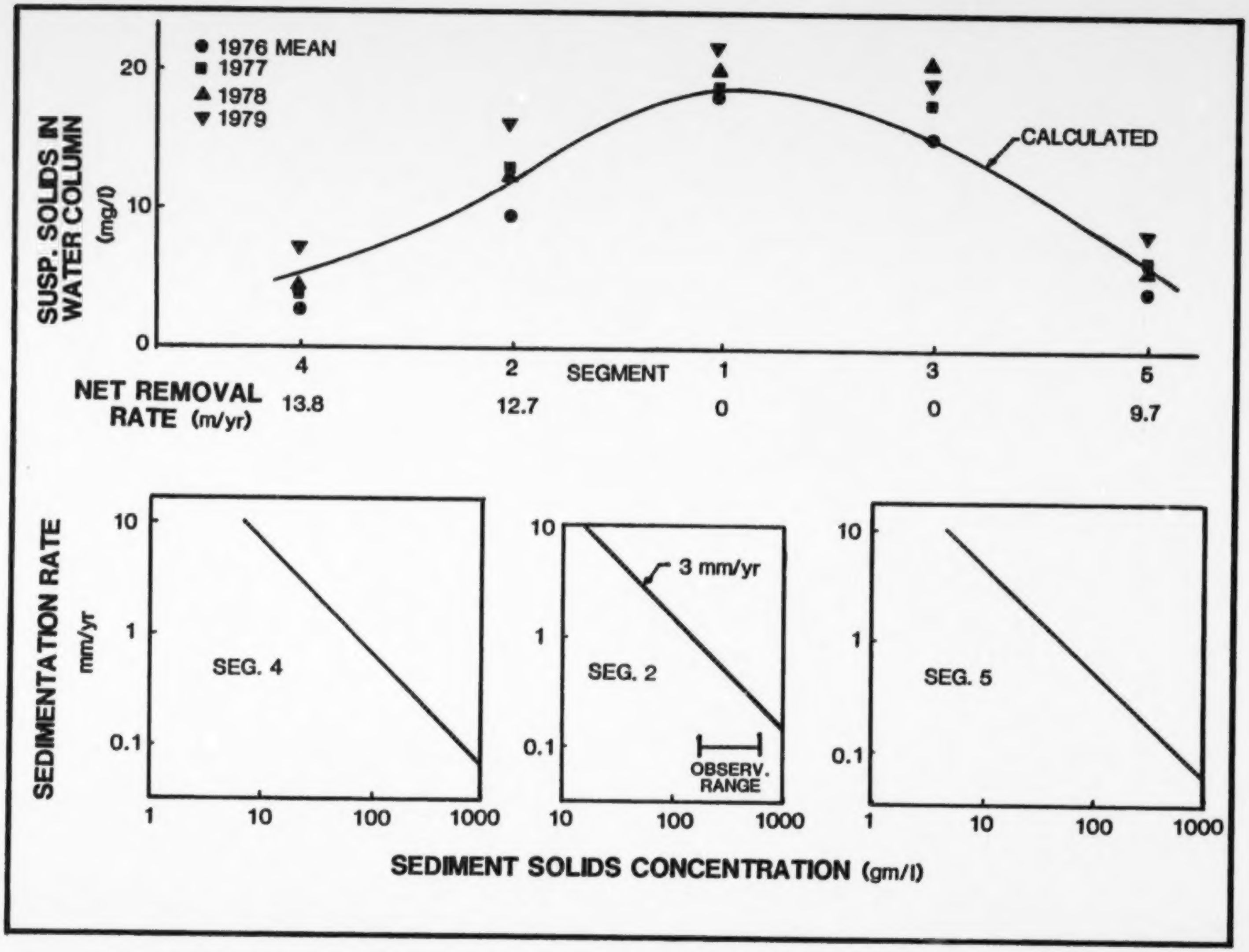
TABLE 4

SEDIMENT SOLIDS CONCENTRATIONS(1) - SAGINAW BAY

	Core Solids Concentrations (mg/l(Bulk)) at Following Depths		
Station(2)	5 cm	12.5 cm	17.5 cm
1A	510,000	1,350,000	1,130,000
6A	250,000	700,000	730,000
11A	230,000	560,000	620,000
24-1	280,000	390,000	507,000
37-1	900,000	1,040,000	730,000
43-1	340,000	420,000	450,000
46-1	280,000	450,000	850,000
50-A	250,000	340,000	420,000
28-A	450,000	790,000	1,070,000
Mean	390,000	670,000	720,000
Std.Dev.	200,000	320,000	240,000

(1) Data from Robbins (1980)

(2) Stations all in Saginaw Bay model segment 2

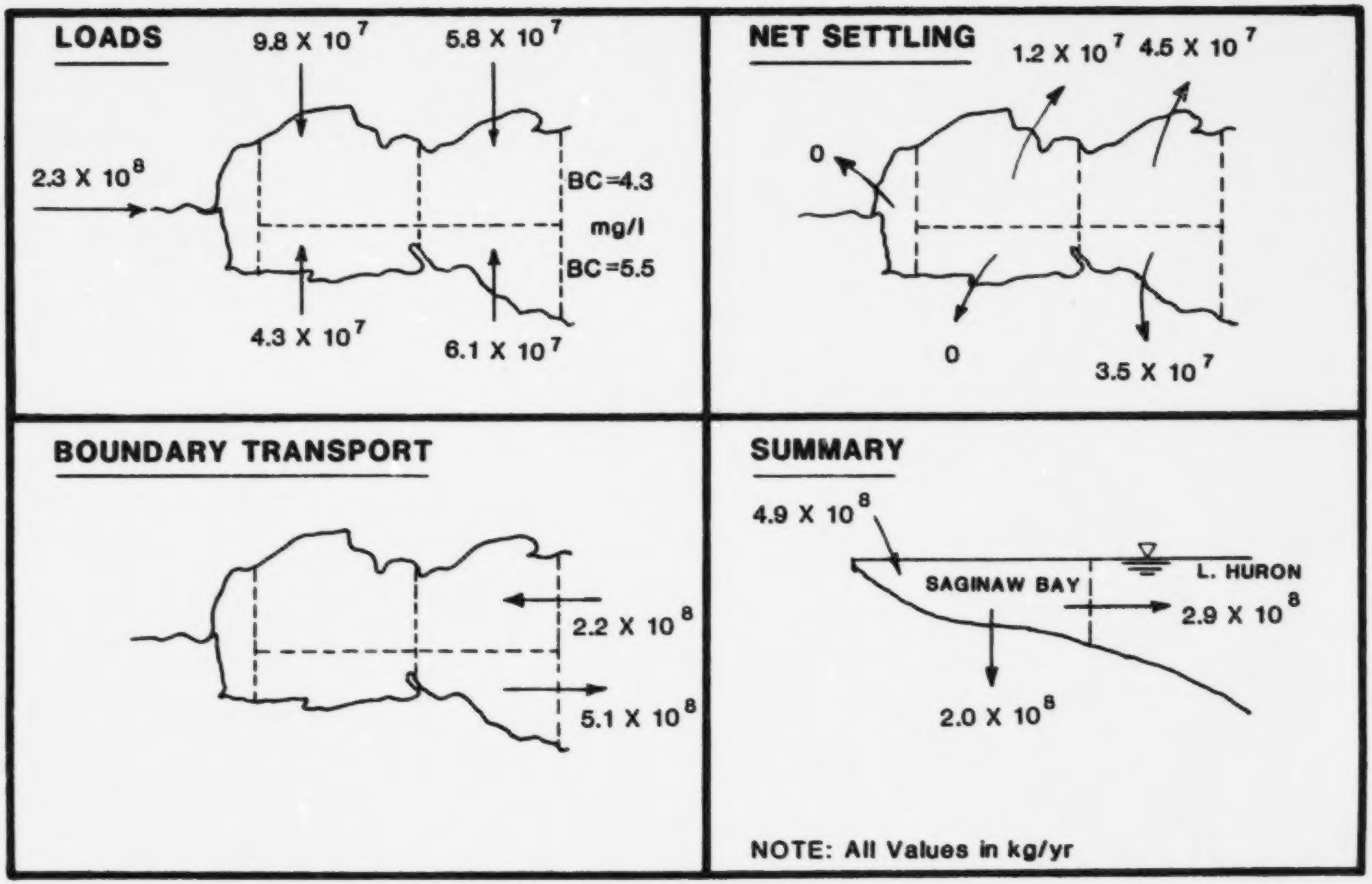


14. Solids calibration using long-term solids data. Data, mean ± 1 Standard Deviation; calculation, solid line.

located primarily in segment 2 of the Saginaw Bay model, a selected number of cores were examined for the sediment solids concentration at the midpoints of a 10 cm well-mixed layer and at the midpoints of two deeper 5 cm layers. The results are summarized in Table 4. For the well-mixed surface sediment layer, sediment concentrations average approximately 390,000 mg/ℓ for nine cores with a range of approximately 230,000 to 900,000 mg/ℓ. This range is shown in Figure 14 for segment 2. If the lower value of the range is used, the corresponding sedimentation rate for the 10 cm well-mixed layer would be approximately 0.8 mm/yr., somewhat less than a previously reported value of 3 mm/yr. (Robbins, 1980).

These results indicate the utility of the simple steady state solids balance. The water column solids data are known in this case with some accuracy and do not exhibit marked spatial gradients. Note that the maximum spatial differences in the average water column suspended solids is about a factor of four. In contrast, the spatial heterogeneity of the sediment is quite marked with regions of deposition, scour and no apparent net deposition. Sediment solids may then vary markedly in the given segment horizontally, but, more importantly, vertically. Boundary layers of sediment solids, i.e. nepheloid or "fluff" layers may be available for interaction with the surface water column at concentrations less than sediment data from cores. Conversely, estimated net sedimentation velocities are often cited only for those regions of deposition and not over an area equivalent to a model segment of Saginaw Bay. The calculation discussed above provides a good estimate of the net flux to the sediment over the entire segment area and sediment solids concentrations is shown in the lower figures of Figure 14. If, as noted above, the solids data from the sediment cores are used, then the net sedimentation velocity varies from 0.25 to 0.8 mm/yr. or almost one order of magnitude less than the 3 mm/yr. previously cited. If, on the other hand, an average net sedimentation over the entire area of segment 2 is fixed at say 3 mm/yr., then the sediment solids concentration that is consistent with that sedimentation velocity is about 45,000 mg/ℓ or one order of magnitude less than the average sediment solids in the top 5 cm of the cores. The results indicate, therefore, that with only the net flux of solids to the sediment (over a segemtn area) known with some confidence, then it is difficult to uniquely specify the net sedimentation or boundary layer sediment solids (or equivalently the boundary layer porosity and solids density as per Eq. (48). Additional tracers (of which the radionuclides or PCBs are examples) would provide additional information that could aid in specifying the net sedimentation and sediment solids concentrations.

A mass balance of suspended solids for the entire model is presented in Figure 15 for three flux categories: the external and internal loads, the net flux removed from the water column and the boundary transport. In the lower right panel, it is seen that 2,970,000 lb/day of solids enter the Bay, 40% (1,190,000 lb/day) is incorporated into the sediments, and the remaining 60% (1,780,000 lb/day) leaves the Bay and enters Lake Huron.


LOADS
9.8 X 10⁷
5.8 X 10⁷
2.3 X 10⁸
BC=4.3
mg/l
BC=5.5
4.3 X 10⁷
6.1 X 10⁷
NET SETTLING
1.2 X 10⁷
4.5 X 10⁷
0
0
3.5 X 10⁷
BOUNDARY TRANSPORT
2.2 X 10⁸
5.1 X 10⁸
SUMMARY
4.9 X 10⁸
SAGINAW BAY
L. HURON
2.9 X 10⁸
2.0 X 10⁸
NOTE: All Values in kg/yr

15. Mass balance of Saginaw Bay total suspended solids under long-term average conditions

PCB CALIBRATION

With the horizontal transport and net loss rate of suspended solids calibrated, analysis of the PCB concentrations can proceed. Total PCB loadings were obtained from U.S. EPA (1982) for 1979, the first year for which total PCB field data were available. As noted in Table 5, the Saginaw River load is approximately 75% of the total load and atmospheric sources contribute an additional 25%. Although open lake concentrations are reported to be in the 1 ng/ℓ range, the boundary condition was selected as 10 ng/ℓ - the value needed to calibrate observed data in segments 4 and 5.

Partition coefficients were selected on the basis of abserved dissolved and particulate fractions and values of 10,000, 50,000, and 100,000 μg/kg per μg/ℓ were selected for segments 1,2, and 3,4, and 5 respectively. These are in accord with values calculated from field measurements, as seen in Table 6. With the partition coefficients selected, the removal rates of total PCBs are then calculated as the particulate fraction of the suspended solids net settling rate (see Eq. (63) for $k_{\ell i} = 0$). Thus, in this calculation, exchange of PCBs with the atmosphere, diffusive exchange with the sediment and decay processes are zero. For segment 2, for example, the net removal rate w_{T2} is:

$$w_{T2} = w_{s2}\ (f_{p2})$$

$$= (12.7)\ (.37) = 4.7\ \text{m/yr.}$$

Similarly, the net total PCBs removal rates for segments 4 and 5 are 4.8 and 3.5 m/yr., respectively.

With the loads, boundary conditions, and net removal rates described above, together with the horizontal transport, the steady state model is used to calculate total PCB concentrations in the water column. The top panel of Figure 16 shows the agreement between calculated values and data observed in 1979. Dissolved and particulate fractions also agree well with observed data, as noted in the next two panels of the figure. The bottom panel displays the particulate PCBs per unit weight of solids and, again, agreement between observed means and calculated values is good for the water column.

In the previous theoretical Section 5 of this report, it was shown that, for zero sediment diffusion and decay the PCBs per unit weight of solids in the water column (r_1) is equal to the sediment toxicant concentrations (r_{1s}). Figure 17 shows this comparison. The upper panel is a reproduction of the bottom panel of Figure 16. Directly below, is a plot of the PCBs in the sediment (r_{1s}), where the solid line is the calculated value of r_{1s} assuming $r_{1s}=r_1$. The data are segment averaged sediment concentrations for 1979, provided by the Grosse Ile Laboratory. Agreement between calculated and observed means is good for segments 1 and 2. It is hypothesized that segment 3 may be a net erosion zone (see suspended solids calibration, Figure 13) in which case the assumption that $r_{1s} = r_1$ is not appropriate.

TABLE 5

ESTIMATED TOTAL PCB LOADING FOR 1979(1)
SAGINAW BAY

Segment	Tributary Loads (lb/day)	Atmospheric Loads (lb/day)	Total Loading (lb/day)
1	1.61(2)	0.05	1.66
2	-	0.16	0.16
3	-	0.07	0.07
4	-	0.12	0.12
5	-	0.12	0.12
Totals	1.61	0.52	2.13

(1)Source: USEPA LLRS Grosse Ile

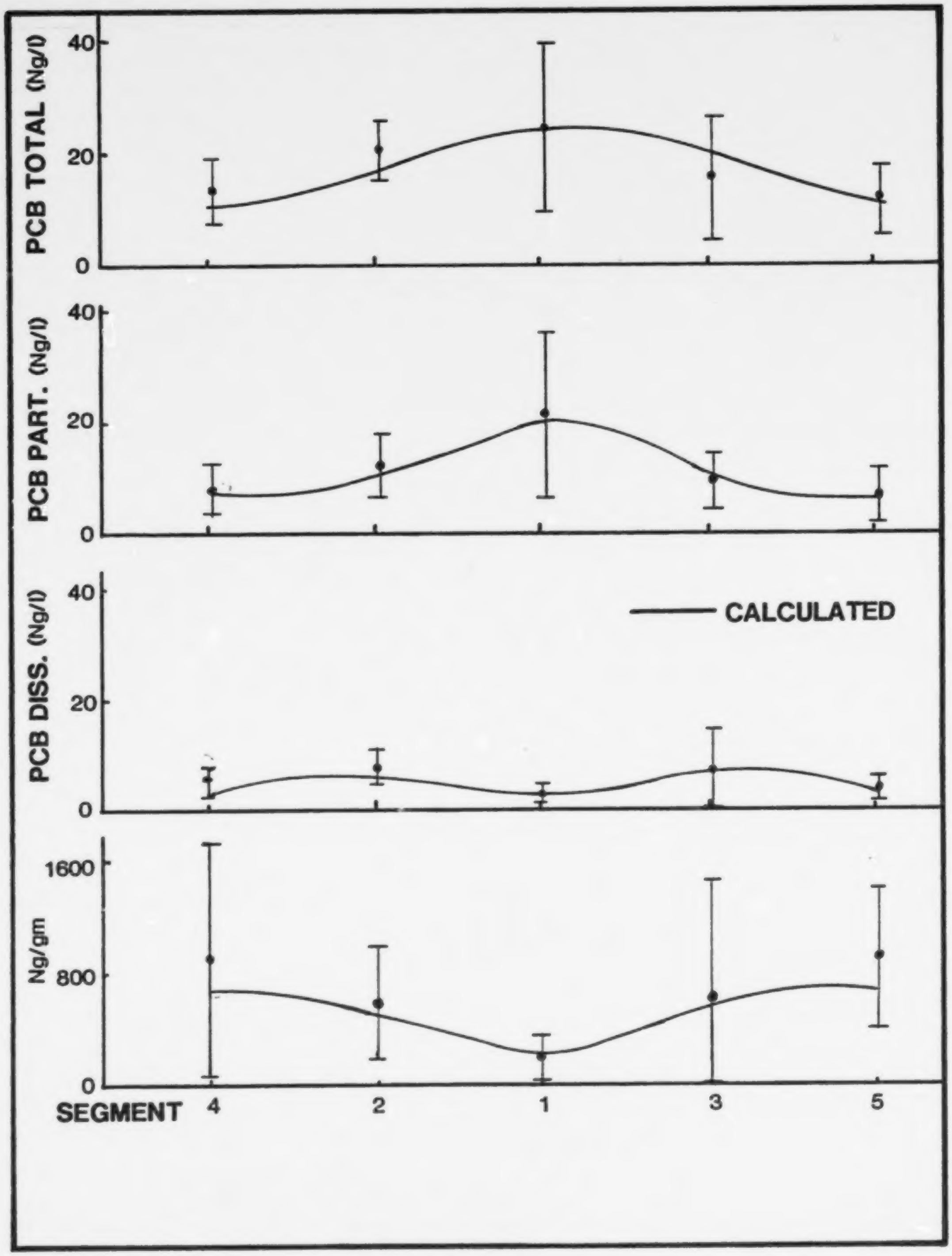
(2)Saginaw River

TABLE 6

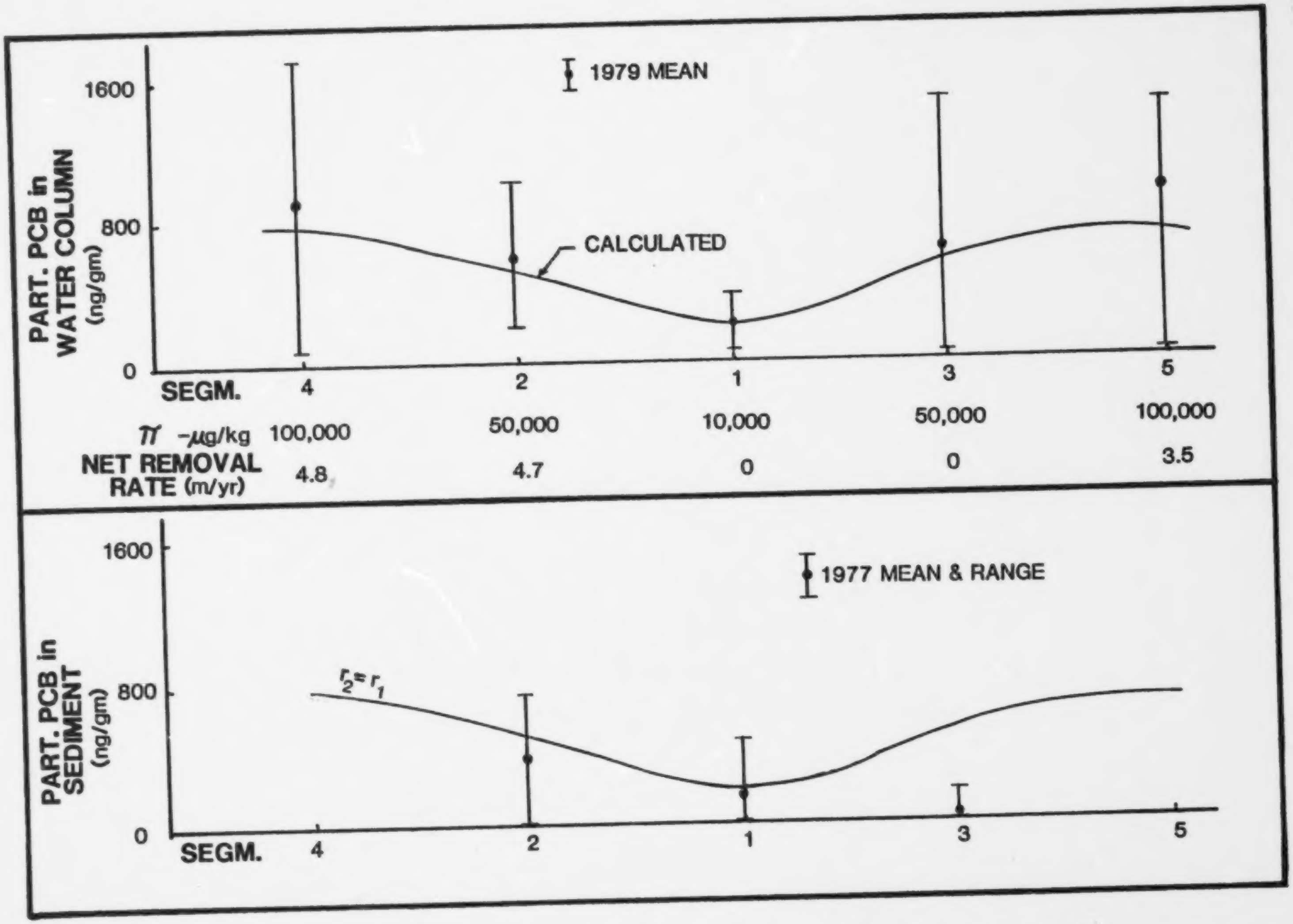
TOTAL PCB PARTITION COEFFICIENTS (1)
SAGINAW BAY

Segment	Partition Coefficient (π) from Observed Concentrations(2)		π Used in
Model	Mean	Approx. Range	
1	10,000	700- 30,000	10,000
2	80,000	7,000-190,000	50,000
3	60,000	20,000-160,000	50,000
4	90,000	10,000-250,000	100,000
5	280,000	10,000-920,000	100,000

(1) All values in μg/kg per μg/ℓ
(2) Data from Grosse Ile Laboratory (1982)



16. Components of PCBs in water column, Saginaw Bay, 1979, Data, mean ± 1 standard deviation; calculation, solid line.



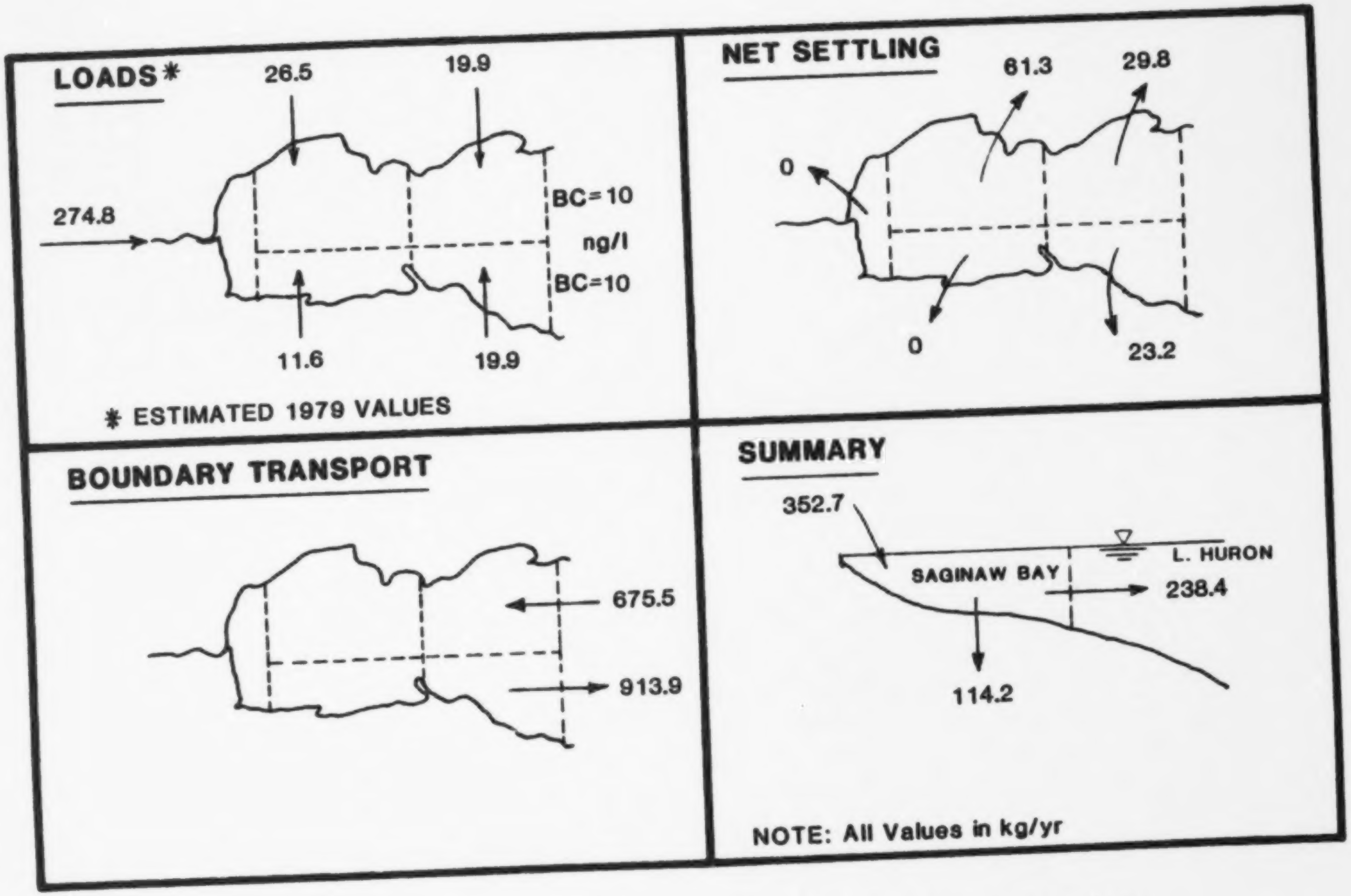
17. Particulate PCB calibration, 1979, water column (upper panel), sediment (lower panel) Saginaw Bay. Data, mean ± standard deviation; calculation, solid line.

A mass balance of total PCBs is shown in Figure 18 for the Saginaw River and atmospheric loads, net settling fluxes and boundary fluxes. As noted in the lower right panel, approximately 30% of the total PCBs entering Saginaw Bay from external loads is incorporated into the sediments of the Bay and approximately 70% is exchanged with Lake Huron.

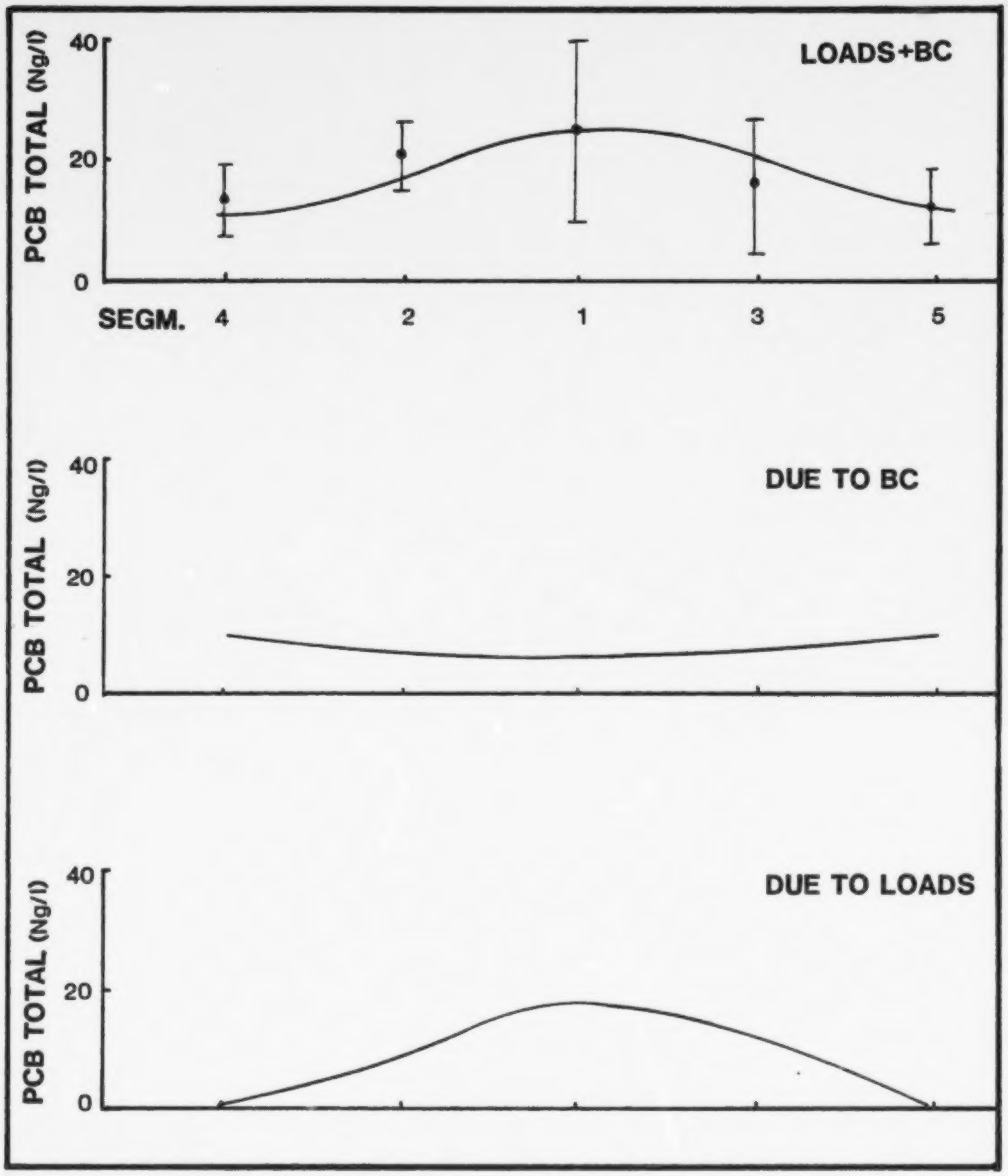
The separate effects of the external PCB loads (Saginaw River and atmospheric) and the boundary conditions are illustrated in Figure 19. The total PCB due to both external loads and boundary conditions is compared with observed data in the top panel of the figure, where the peak concentration in segment 1 is seen to be approximately 24 ng/ℓ. Of the 24 ng/ℓ, approximately 6 ng/ℓ is due to the boundary condition (center panel) and the remaining 18 ng/ℓ is the effect of the loads. Thus, complete removal of the Saginaw River loads and maintenance of the boundary at 10 ng/ℓ would result in at least a 75% reduction in the segment 1 PCB concentration under this new steady-state condition. Additional reduction would occur since some significant fraction of the boundary concentration is probably caused by the loads. Therefore, reducing the boundary concentration to lower open Lake Huron levels would reduce the concentration in segment 1. If, for example, the boundary decreased to a value of 5 ng/ℓ, the concentration in segment 1, under the no-load situation, would be approximately 3 ng/ℓ.

A mass balance of PCBs for the external loads alone (Figure 20) shows that approximately 10% of the load entering the Bay is incorporated in the sediment and 90% enters Lake Huron - the bulk of it from segment 5. A similar balance for the boundary condition reveals a net source from Lake Huron into segment 4, and a net sink into the Bay sediments before the remaining mass returns to Lake Huron from segment 5 (Figure 21).

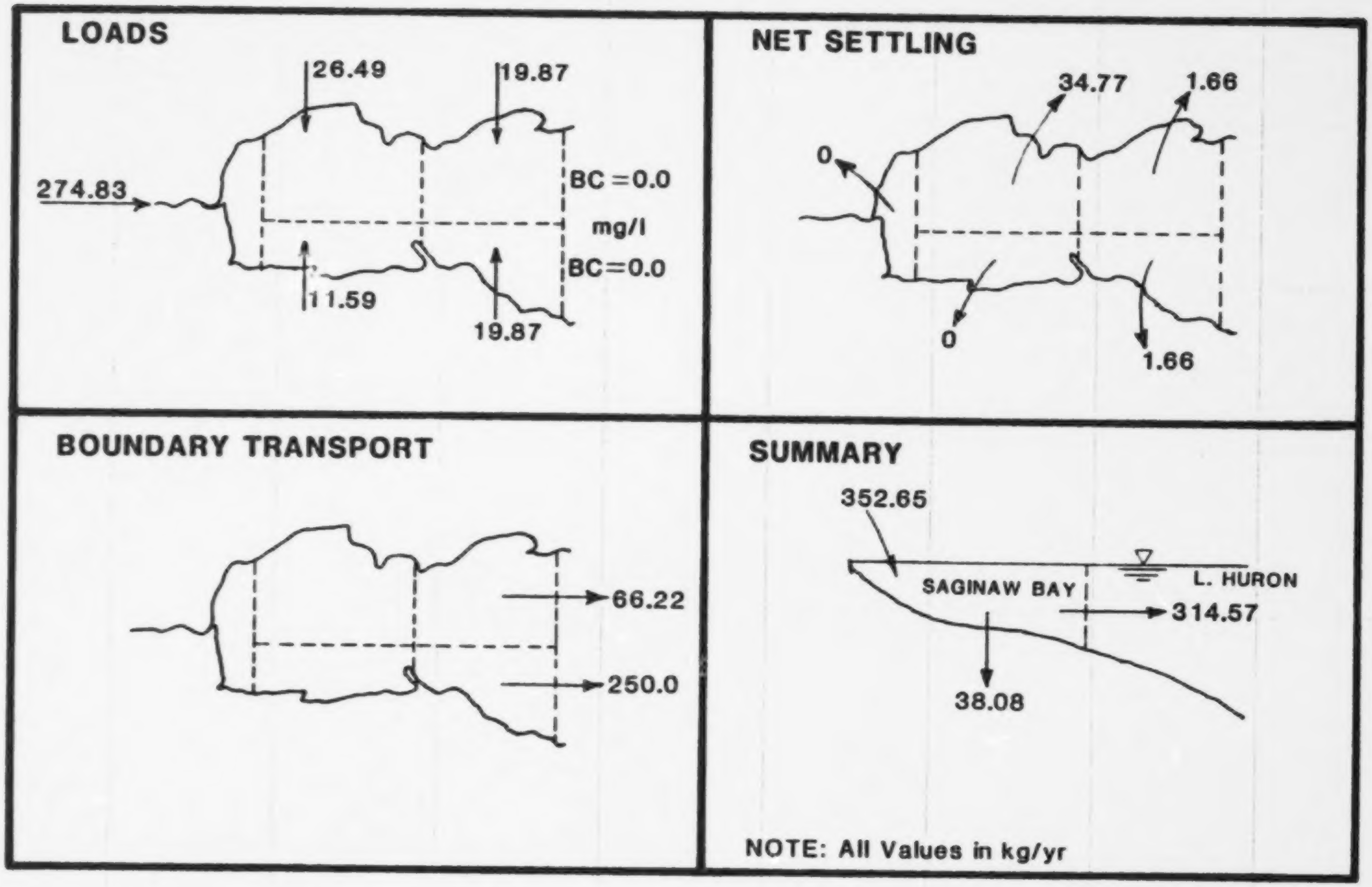
This steady state analysis, therefore, provides a reasonable approximation to the observed data with a minimum amount of parameter specifications. Indeed, as noted previously, by virtue of the steady state analysis, it is not necessary to specify the solids settling and resuspension velocities. Only the net loss of solids is required. Additional analyses of the role of PCB volatilization and sediment diffusion due to variable partition coefficients would also prove useful in further describing the distribution of PCB in the Bay. Finally, a steady state model evaluation of the distribution of the various PCB isomers, representing a range of chemical behavior would increase the overall credibility of the modeling framework.


LOADS*
26.5
19.9
274.8
BC=10
ng/l
BC=10
11.6
19.9
* ESTIMATED 1979 VALUES
NET SETTLING
61.3
29.8
0
0
23.2
BOUNDARY TRANSPORT
675.5
913.9
SUMMARY
352.7
L. HURON
SAGINAW BAY
238.4
114.2
NOTE: All Values in kg/yr

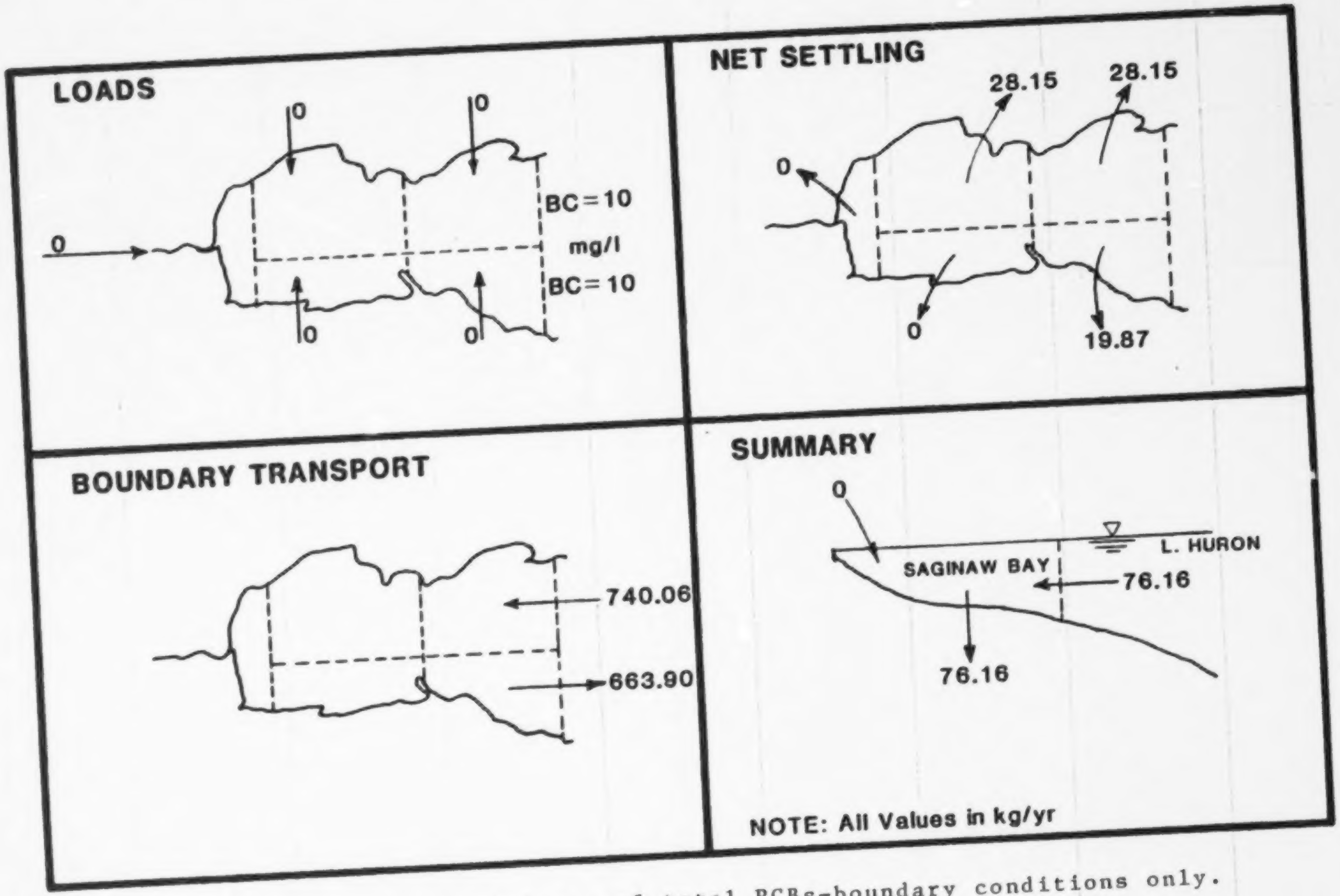
18. Mass balance of total PCBs for Saginaw Bay under long-term average conditions



19. Effects of external loads and boundary conditions on total PCB average concentrations in water column of Saginaw Bay


LOADS
274.83
26.49
19.87
BC=0.0
mg/l
BC=0.0
11.59
19.87
NET SETTLING
34.77
1.66
0
0
1.66
BOUNDARY TRANSPORT
66.22
250.0
SUMMARY
352.65
SAGINAW BAY
L. HURON
314.57
38.08
NOTE: All Values in kg/yr

20. Saginaw Bay mass balance of total PCBs-external loads only.


LOADS
0
0
0
0
0
BC=10
mg/l
BC=10
NET SETTLING
28.15
28.15
0
0
19.87
BOUNDARY TRANSPORT
740.06
663.90
SUMMARY
0
L. HURON
SAGINAW BAY
76.16
76.16
NOTE: All Values in kg/yr

21. Saginaw Bay mass balance of total PCBs-boundary conditions only.

SECTION 7

GREAT LAKES MODEL CALIBRATION

INTRODUCTION

Radionuclide Models

A credible analysis of toxicant fate and response should draw on existing data for testing and comparison purposes - such data are not yet available in any consistently accurate form for many contemporary toxic chemicals. Information on input loads is sparse and data on water column levels have been subject to wide variability, due principally to changes in analytical techniques.

However, relatively complete data sets exist for some radionuclides such as those associated with previous weapons testing. Examples include plutonium-239 and cesium-137. Data on input loads (principally atmospheric) are known or can be estimated over a period of several decades. In addition, much work on the fate of ^{239,240}Pu and ^{137}Cs in the water column, sediments and food chain has been accomplished through the Argonne National Laboratory (e.g. Edgington, et al. 1976; Robbins and Edgington, 1975; Wahlgren and Nelson, 1975; Wahlgren and Marshall, 1975; Wahlgren, et al., 1981). The models utilized by these investigators are generally of two types. In the first type, sediment flux models are constructed where the focus is on modeling the depositional flux of a chemical, resulting sedimentation rate and comparison to sediment core data. For example, Edgington and Robbins (1976) modeled the deposition of lead to the Lake Michigan sediments where Eq. (22) was solved for the net depositional flux of lead given by $w_T c_T$. In earlier work on plutonium and cesium in Lake Michigan, Edgington and Robbins (1975) focused their modeling effort on the sediment core data using a version of Eq. (23) where from the available sediment data estimates were derived of the flux of plutonium and cesium delivered to the surface sediment layer. This sediment flux is related to the external load via introduction of a "flux normalization factor" which incorporates the interactions shown in Eq. (22).

The second type of model is focused on the behavior of radionuclides in the water column. For example, Wahlgren, et al. (1981) present a time variable model that considers the net loss from the water column as a single parameter. The model equation used replaces all sediment interaction terms on the right side of Eq. (22) with an overall apparent settling velocity. Plutonium data from the Great Lakes are then used to obtain estimates of this net loss parameter. In general, however, it is seen that for the time variable case only if there is no interaction with the sediment can one obtain the single equation with a single loss parameter. At steady state, however, as shown in Eq. (61), such a single loss parameter (w_T) does result and incorporates sediment interactions as noted previously.

It is precisely the dynamic behavior of chemicals that sometimes is of importance as in questions related to the length of time required for the lakes to respond to external reductions (or increases) in chemical input. The mechanisms of sediment interaction, partitioning and exchange then become important in estimating the time variable behavior of a body of water. The difficulty with the previous models of radionuclide behavior in the Great Lakes is the lack of inclusion of those fundamental mechanisms which would permit extension of the model to other chemicals.

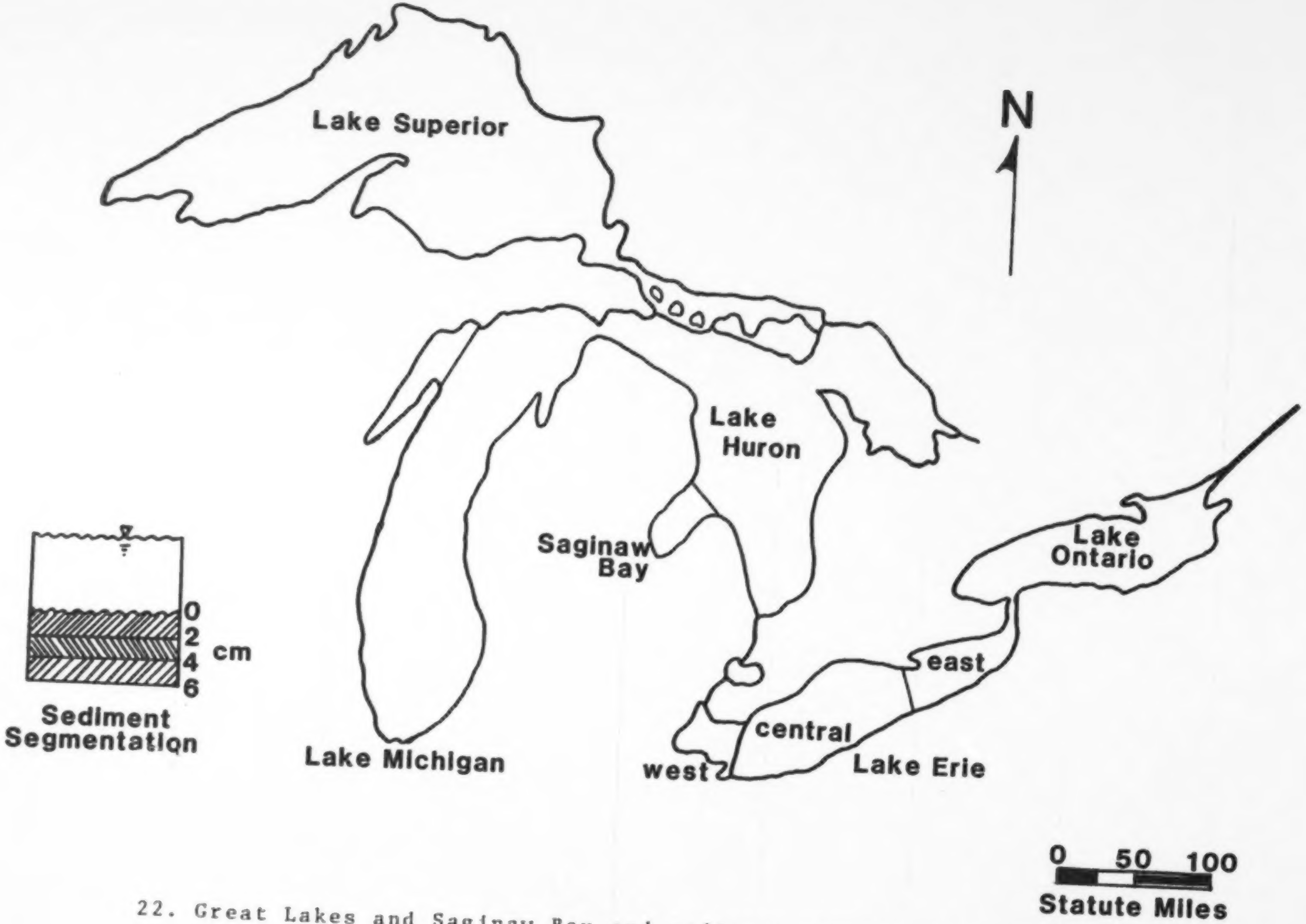
This difficulty of previous models is also recognized by Chapra (1982) in his work. The model of Chapra follows similar lines to that developed and applied here and Chapra also included the use of radionuclides as a calibrating variable for a toxicant model for the Lakes. The resuspension of sediment particulates into the water column however was not explicitly included in the calibration of the model to the radionuclide data. In the model discussed here, therefore, emphasis is on application of the theory presented previously which incorporates the partitioning and sediment interactions into a more complete and general framework. Since plutonium sorbs to particulate matter, does not volatilize or appreciably decay, it becomes a useful water quality variable for calibration. Following the calibration, the model is then further applied to the PCB problem context in the Lakes.

Model Segmentation

Since the time scale of the model is considered to be long term, i.e. year to year, the physical segmentation of the model considers the Lakes to be completely mixed with the exception of Lake Erie (Figure 22). This Lake is divided into three basins: west, central, and east to reflect varying regions of solids deposition and water column solids concentrations. In addition, Saginaw Bay is included as a separate embayment from Lake Huron to represent a more local region interacting with a large lake. Table 7 shows the physical parameters used in the model. Three sediment segments of 2 cm each in depth are included under each of the lakes or region of lake. This results in a model with eight water column segments and twenty-four sediment segments for a total of thirty-two segments.

Calibration Procedure

The suspended and sediment solids are considered to be at steady state so that Eqs. (43) and (49) are appropriate. As noted in the toxicant equations (Eqs. 50-51) it is necessary that the solids concentrations be known (for calculation of the fraction of the chemical sorbed to particulates, f_p) as well as the settling and resuspension velocities of the solids. As such, overall flux balance or solids budget estimates do not provide the level of detail necessary for the general chemical model. On the otherhand, it is not possible to uniquely calculate the solids concentration in the open waters of the Great Lakes because of uncertainty in the settling and resuspension velocities, the external solids loading and even the water column solids concentrations. Thus, the use of a variable such as plutonium in the chemical model is essen-


Lake Superior
N
Lake Huron
Lake Ontario
Saginaw Bay
0
2
4
6
cm
Sediment Segmentation
Lake Michigan
east
central
west
Lake Erie
0 50 100
Statute Miles

22. Great Lakes and Saginaw Bay and sediment segmentation used in model.

TABLE 7

GEOMETRIC AND TRANSPORT PARAMETERS OF WATER COLUMN USED IN GREAT LAKES MODEL

Lake or Region	Volume km^3	Depth m	Surface Area km^2	Flow		Horizontal Exchange m^2/s
				In m^3/s	Out m^3/s	
Superior	11,326	137	82,882	2,033	2,033	-
Michigan	4,716	82	57,772	1,470	1,470	-
Huron	3,243	56	57,437	3,503	4,967	-
Saginaw Bay	25	6	4,222	153	153	1,229
Erie-West	23	8	3,026	4,967	5,282	4,425
-Central	288	18	15,716	5,282	5,517	23,354
-East	175	28	6,254	5,517	5,692	
Ontario	1,666	86	19,485	5,692	6,740	-

tially for calibration of solids interactions rather than as a calibration of plutonium itself.

Accordingly, the calibration procedure proceeded along the following lines. (a) A review was made of data on fine grain solids loading to the Lakes, net depositional flux of solids, and water column suspended solids concentrations. Since the solids model is considered as steady state, Eq. (45) was used to provide first estimates of w_n, the net loss rate of solids from the water column. From assigned porosity in the surface sediment layer, particle density and net flux of solids to the sediment, the net sedimentation rate is computed from Eq. (48). (b) With the estimate of the net loss of solids, w_n, a range of particle settling velocities were assigned and the resuspension velocity necessary to maintain the solids balance was computed from Eq. (44) as

$$w_{rs} = w_s \left(\frac{w_a}{w_n} - 1\right) \tag{72}$$

(c) Since there are an infinite number of combinations of settling and resuspension velocities that will result in the same solids balance, an additional calibrating variable is needed. For the solids concentration, net loss rate and assigned settling and resuspension velocities, the time variable chemical model with sediment interaction (Eqs. 22-23) was numerically solved using plutonium as the calibrating variable. All decay mechanisms and sediment diffusion were assumed to be zero and a sensitivity analysis using three values of plutonium solids partitioning was conducted. (d) The plutonium calculation was therefore used to evaluate the settling and resuspension parameters of the lakes for use in subsequent calculations of other chemical concentrations.

SOLIDS BALANCE

As noted previously, the toxic chemical model interacts with the solids concentrations in both the water column and sediment. The degree of chemical partitioning on to particulates determines the importance of the solids concentration in the fate of the toxicant. It is relevant then to undertake a gross solids balance for the Great Lakes to estimate settling and resuspension velocities and the net loss rate of solids to the sediment. The first step is the estimation of external solids loading. The results of using these loads in a simplified steady state calculation and a steady state model using the preceding segmentation are then given and discussed.

Suspended solids loading to the Great Lakes results from many sources. Tributaries and shoreline erosion, and atmospheric inputs are important loads of solids to the Lakes. Direct input of municipal and industrial sources are generally insignificant on a Great Lakes scale.

Erosion and Tributary Loads

The principal sources for estimating the solids loading due to shoreline erosion are Monteith and Sonzogni (1976), (drawing on the work

TABLE 8
ESTIMATED SHORELINE EROSION AND TRIBUTARY SOLIDS LOADING RANGE[1]

(All Units in 10^6 mt/yr)

Lake	Shoreline Erosion U.S.	Shoreline Erosion Can.	Shoreline Erosion Total	Tributary U.S.	Tributary Can.	Tributary Total	Total Erosion & Tributary	Soil Erosion % of Total
Superior	4.6-18.3 (11.3)[2]	4.1-16.2[3]	9.7-34.5	0.7-1.4	1.5-3.0	2.2-4.4	11.9-38.9	82-89
Michigan	7.8-40.0 (21.8)[2]	-	7.8-40.0 (21.8)	0.6-0.7	-	0.6-0.7	8.4-40.7	93-98
Huron	0.4- 2.8 (1.3)[2]	0.3- 1.0	0.7- 3.8	0.5-0.8	1.0-1.7	1.5-2.5	2.2- 6.3	32-60
Erie	1.4- 7.3 (4.0)[2]	8.7-14.0	10.1-21.3 (25.4)[4]	6.0	2.1	8.1	18.1-33.5	56-64
Ontario	0.5- 2.9	1.2- 1.4	1.7- 4.3	1.0-1.5	0.6-1.0	1/6-2.5	3.3- 6.8	52-63

[1] Based on Monteith and Sonzongni (1976), Thomas and Haras (1977), and Sonzongni, et al. (1978)

[2] Estimated average (Monteigh and Sonzongni, 1976)

[3] Estimated based on average U.S. loading per km shoreline

[4] Estimated by Apmann (1975)

of Seibel, et al., (1976), and Thomas and Haras (1977). These estimates vary widely and reflect the substantial difficulty in estimating this source of solids. Monteith and Sonzogni, (1976) gave shoreline erosion loads by county for the United States shoreline. Erosion varies widely from county to county, with Lake Michigan having the highest loading rate per kilometer of shoreline, followed by Superior, Erie, Ontario, and Huron respectively. The range of shoreline erosion loads is shown in Table 8. With respect to the character of the eroded material, Monteith and Sonzogni (1976) report that of the total average annual volume of shoreline material eroded, 53% is estimated to be "sandy material," 34% is estimated to be "loamy material," and 13% is estimated to be "clayey material." On a lake by lake basis, Monteith and Sonzogni (1976) estimate the values shown in Table 9.

TABLE 9
ESTIMATED PERCENT OF SOIL TYPES
IN SHORE EROSION LOADS
(From Monteith and Sonzogni, 1976)

		Percent	
Lake	Sand	Loam	Clay
Superior	17	43	40
Michigan	75	23	2
Huron	57	43	0
Erie	44	40	16
Ontario	15	74	11
Total	53	34	13

Tributary loading of solids are estimated by Sonzogni, et al., (1978) and also tend to be quite variable due to the difficulty in estimating input loads from a tributary where only occasional grab samples of solids concentrations are available. Estimates of tributary loads are obtained by a ratio of the Canadian tributary drainage areas given in IJC (1978). Table 8 shows the estimated loading ranges.

As shown in Table 8, shoreline erosion loads relative to tributary loads are most significant for Lake Michigan and Table 8 indicates that for Michigan, about 75% of the shoreline erosion load is of a sandy material. The shoreline erosion loads are, therefore, of significance and reflect an important source of solids to the lakes. However, because of the sandy nature of these solids, the impact is probably more local and near-shore due to high settling velocities. The range in the estimates should be carefully noted and variations in the loadings for a given year and specific location may be expected.

Table 10 shows the areal solids loading rate of fine grain solids used in the model calculation below. These loadings were arrived at by (a) determination of solids concentration in the lake giving the term QM in Eq. (43), (b) evaluation of the net depositional loading of solids

TABLE 10

SOLIDS LOADING, CONCENTRATION AND NET SOLIDS LOSS RATES USED IN MODEL

Lake/ Region	Fine Grain Solids Loading Rate g/m^2-yr(1)	Overflow Rate m/yr.	Solids Conc. mg/l	Net solids Loss Rate m/yr(m/d)	Net Sed. Depos.Rate g/m^2-yr	Net Sed. Vel.(4) mm/yr
Superior	98	0.8	0.5	195(0.53)	98	0.41
Michigan	69	0.8	0.5	137(0.38)	69	0.29
Huron	109	3.4	0.5	213(0.58)	107	0.45
Saginaw Bay	146	10.3(2)	8.0	8(0.02)	64	0.27
Erie-West	3762	101.1(3)	20.0	87(0.24)	1740	7.24
Central	1414	66.8(3)	5.0	216(0.59)	1080	4.52
East	1658	146.5(3)	5.0	185(0.51)	927	3.87
Ontario	229	11.0	0.5	447(1.22)	224	0.93

(1) Includes upstream loads and turbulent exchange loads
(2) Includes turbulent exchange with Lake Huron
(3) Includes turbulent exchange between Lake Erie basins
(4) Using porosity of surface sediment = 0.9 throughout ρ_s = 2.4 and and Eq. (9); porosity = 0.85 and 0.82 for 2-4 cm and 4-6 cm sediment layers respectively.

(discussed below) which yields the quantity $w_p m$ in Eq. (43), (c) estimation of external load from the previously discussed source so that a steady state consistent mass balance was achieved. Actually, in the toxics model, the external load of solids is not really needed; only the concentration and net depositional velocities are required. The loadings shown however in Table 10 are within the reported ranges from Tables 8 & 9.

Suspended Solids Concentrations

Open lake suspended solids concentrations were difficult to estimate since data reported in the U.S. EPA STORET system included a lower bound of 1.0 mg/ℓ thereby resulting in apparently unrealistically high average levels. Turbidity levels appeared more realistic based on solids concentrations measured at low levels for Lake Ontario by Nriagu, et al. (1981) who reported average open lake concentration of 0.5 mg/ℓ. Torrey (1976) reported that of 170 samples collected, 10 km offshore in Lake Michigan, only 20% were greater than 1 mg/ℓ of suspended solids. Also, for southern Lake Michigan, Chambers and Eadie (1981) give results for a cross section from Grand Haven, Michigan to Milwaukee, Wisconsin during August, 1979. Excluding the solids concentration very close to the bottom, the average suspended solids concentration in the water column was 0.8 mg/ℓ with a standard deviation of 0.47 mg/ℓ. Finally, IJC (1979) indicated that solids concentrations for the open water of Lake Superior is about 0.2 mg/ℓ. Average turbidity levels as reported in the STORET data base range from 0.3-0.6 (JTU) for Lakes Superior, Michigan, Huron, and Ontario, and of course range upward to 20-25 JTU for the more turbid western and central Lake Erie. Considerable variation from year to year and for near shore regions throughout the year are to be expected. Hall (1980) has examined these variations for southern Lake Michigan and Figure 23 is a plot of the year to year variation in turbidity at the Chicago water intake.

Also, Hall (1980) in an analysis of the relationships between suspended solids and turbidity data for Lake Michigan shows that for turbidity less than 1 JTU, the solids concentrations is almost linear to the turbidity. As a result of these reported levels and from a balance between reported net depositional fluxes of solids, suspended solids concentration that were used are shown in Table 10. It should be noted that overall, the data on open lake suspended solids concentrations are generally weak and more data need to be obtained.

Sediment and Sedimentation Rates

A very large literature exists for the sediments of the Great Lakes. There is no intention here to exhaustively review that literature. For the purposes of the overall preliminary model, some ranges of net sedimentation velocity and sediment solids fluxes and porosity are sufficient. Table 11 summarizes the reported values for the open Lakes and some regions of the Lakes. As noted, the range within a lake is very large reflecting heterogeneous regions of deposition. The Western and Eastern basins of Lake Erie are shown to have the highest flux and net sedimentation rates. These fluxes and sedimentation velocities generally reflect the fine grain solids.

TABLE 11
REPORTED RANGE OF SOLIDS FLUX AND NET SEDIMENTATION RATES FOR GREAT LAKES

Lake		Range of Solids Flux to Sediments g/m^2-yr	Range of Net Sedimentation Rate (mm/yr)	Reference
Superior-	N.W.Basin	155-3040	0.6-2.8	1
	Central	50- 255	0.2-1.0	1
	Southern	25- 700	0.1-2.3	1
Michigan		60-1015	0.2-3.2	2
Huron -		65- 495	0.3-2.2	3
	Georgian	35- 90	0.2-0.4	3
	Saginaw Bay	780	3.1	3
Erie -	West	830-6450	1.7-7.4	4
	Central	150- 790	0.8-1.7	4
	East	40-3790	0.2-8.5	4
Ontario		85-1225	0.3-2.2	5

1. Kemp, et al. (1978)
2. Edington and Robbins (1976)
3. Kemp and Harper (1977)
4. Kemp, et al. (1977)
5. Kemp and Harper (1976)

Porosities of sediment samples also vary widely. For example, Robbins and Edgington (1975) for Lake Michigan show porosities of 0.9 at 1 cm to 0.86 at 32 cm for one core and 0.86 at 1 cm to 0.75 at 32 cm for another core.

With the estimate of solids loading and concentration and the overflow rate, q, the net loss rate of solids w_n was computed from Eq. (72). In order to "close" the solids balance, the net depositional flux calculated from this solid balance was compared to estimates from sediment analyses and budget estimates as shown in Table 11 and reported for Lakes Superior, Huron, Erie, and Ontario by Kemp, et al. (1976, 1977a,b, 1978), Evans, et al. (1981) and for Lake Michigan by Edgington and Robbins (1976). The complete steady state solids balance, resulting net loss rates from the water column and net sedimentation are given in Table 10. The net loss rates range from 8 m/yr. for the shallow Saginaw Bay to 487 m/yr. for Lake Ontario.

PLUTONIUM-239 CALIBRATION

With the estimates of the net loss rate of solids and associated concentration, the time variable model given by Eqs. (22) and (23) was applied to the fate of plutonium in the Grat Lakes using the settling velocity of the particulates as a parameter and calculating the resuspension velocity from Eq. (72) to maintain the solids balance. The settling velocity, w_a, was set at one of three levels: $w_a = w_n$ (i.e. no resuspension) $w_a = 2.5$ m/d, and $w_a = 5.0$ m/d.

The partition coefficient for plutonium must also be specified. Table 12 summarizes some of the reported coefficients. The reported range for algae, inorganic solids and marine sediment (Noshkin, 1972; Hetherington, et al., 1975; Marshall, et al., 1975; Thompson, 1975; Hetherington, 1978; as well as from Wahlgren and Nelson, 1976 and Edgington, et al., 1979 is from about $10^{4.5}$ to 10^{6} ℓ/kg. Hetherington (1978) showed some dependence of the partition coefficient with particle size and reported values of about $10^{5.5}$ ℓ/kg for particles from 1-10 μm and then a decrease to about $10^{4.5}$ for particles from 10 μm to about 70 μm. As a result of the range of reported values, levels of 150,000-400,000 and 10^{6} ℓ/kg were investigated as part of the sensitivity analysis to partition coefficient.

For the calculations, the external plutonium input was as given by Wahlgren, et al. (1981) with a constant loading from 1973 to 1977. Figure 24 shows the time history of the plutonium load. As shown, peak loadings occurred in the late 1950's and early 1960's corresponding to increased weapons testing during that period. Unfortunately, water column data were not collected during this time, but began in 1971. Sediment core data have, however, been obtained in Lake Michigan and as noted below can form a basis for calibrating the time variable model over the entire load history. Only the atmospheric input was considered. Wahlgren, et al. (1981) discuss the potential importance of the plutonium contribution from watershed runoff although lack of data on tributary concentrations precludes an accurate assessment of this source. At 0.5-1.0 fci/ℓ in tributary waters (Wahlgren, et al., 1981),

TABLE 12

SOME PARTITION COEFFICIENTS FOR ^{239}PU

Partition Coefficient Bq/kg(d)÷Bq/ℓ	Type and or Location	Reference
$10^{4.5}-10^{5.5}$	Marine Sediment; Irish Sea	Hetherington (1978)
$10^{5}-10^{6}$	Algae, seston; Rocky Flats, Utah	Thompson (1975)
$10^{4.5}-10^{5}$	Particulates, Phytoplankton; Great Lakes	Marshall, et al. (1975)
$10^{4.5}$	Algae; No. East Irish Sea	Hetherington, et al. (1975)
$10^{4.3}$	Algae; Oceanic	Noshkin (1972)

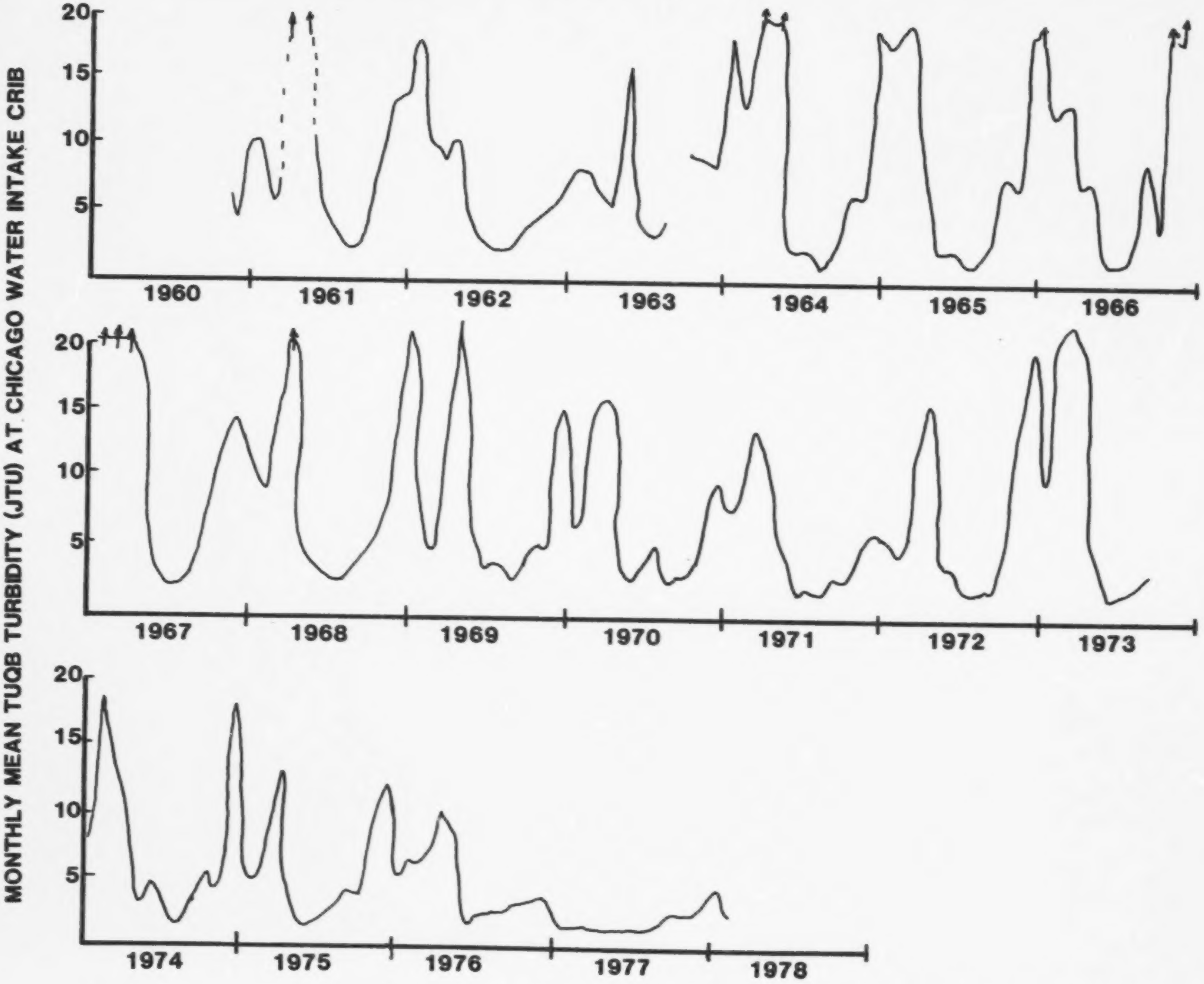
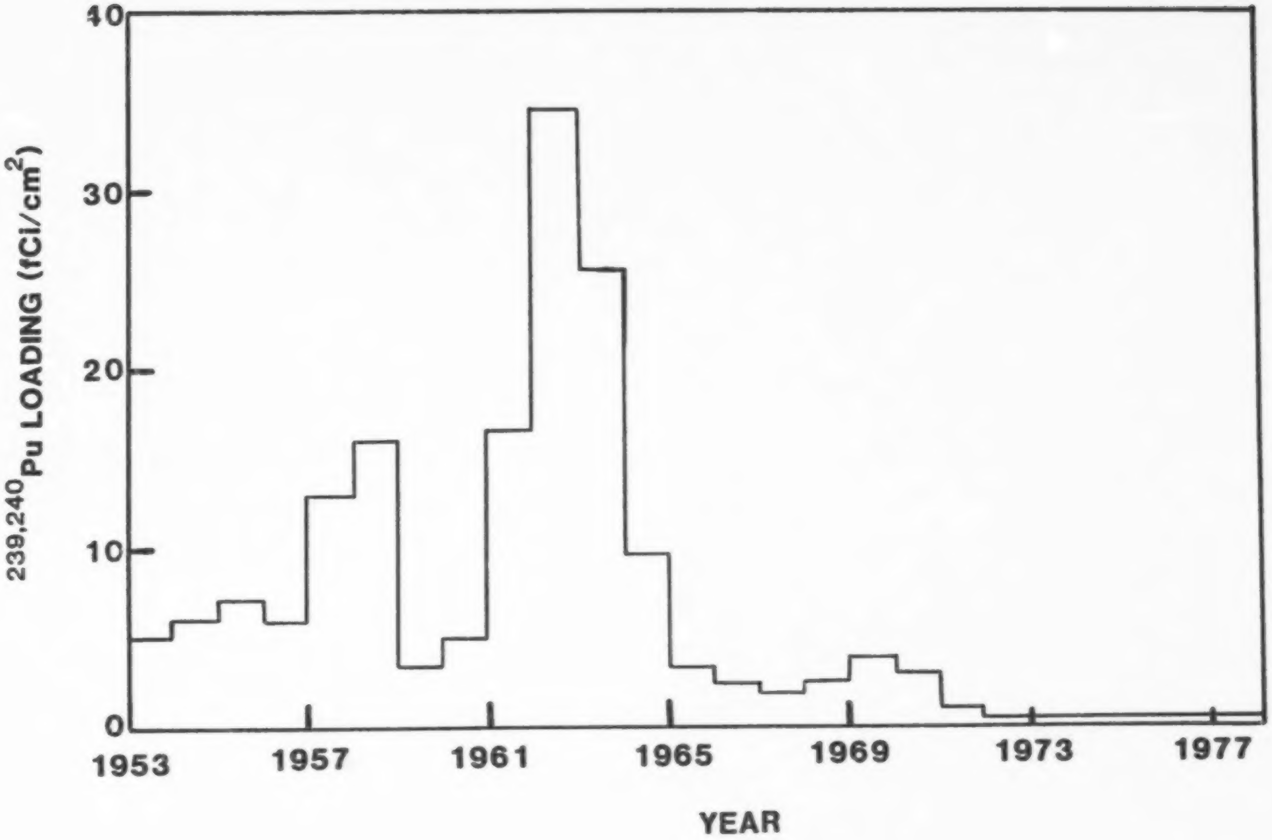


Figure 23 . Long term variations in turbidity at Chicago water intake(after Hall, 1980).



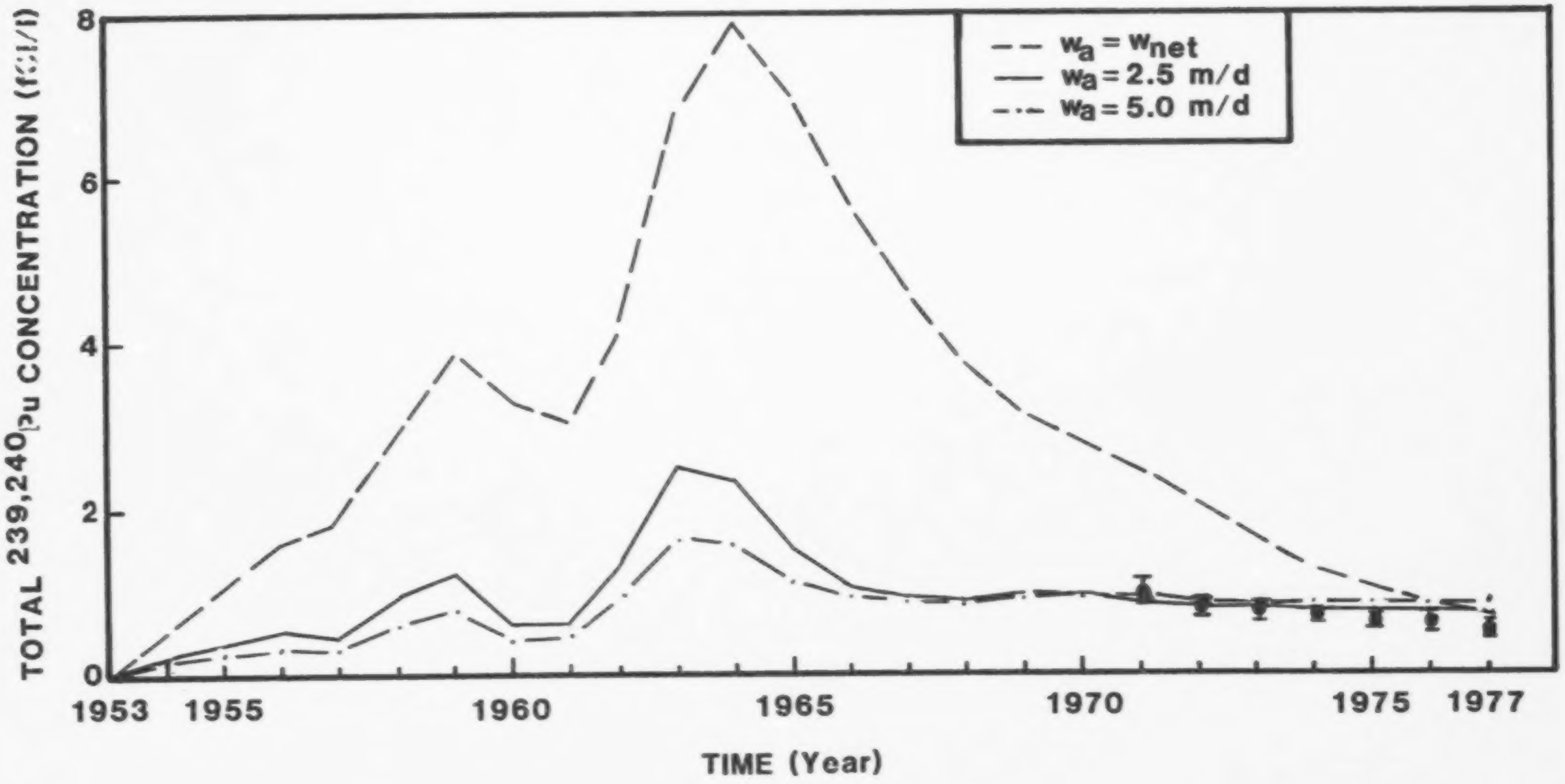
24. Annual areal deposition of ^{239,240}Pu loading to Great Lakes (from Wahlgren, et al., 1981), with constant loading 1973-1977.

however, the runoff input ranges from 1-8% of the total atmospheric 1970's load to Lake Michigan.

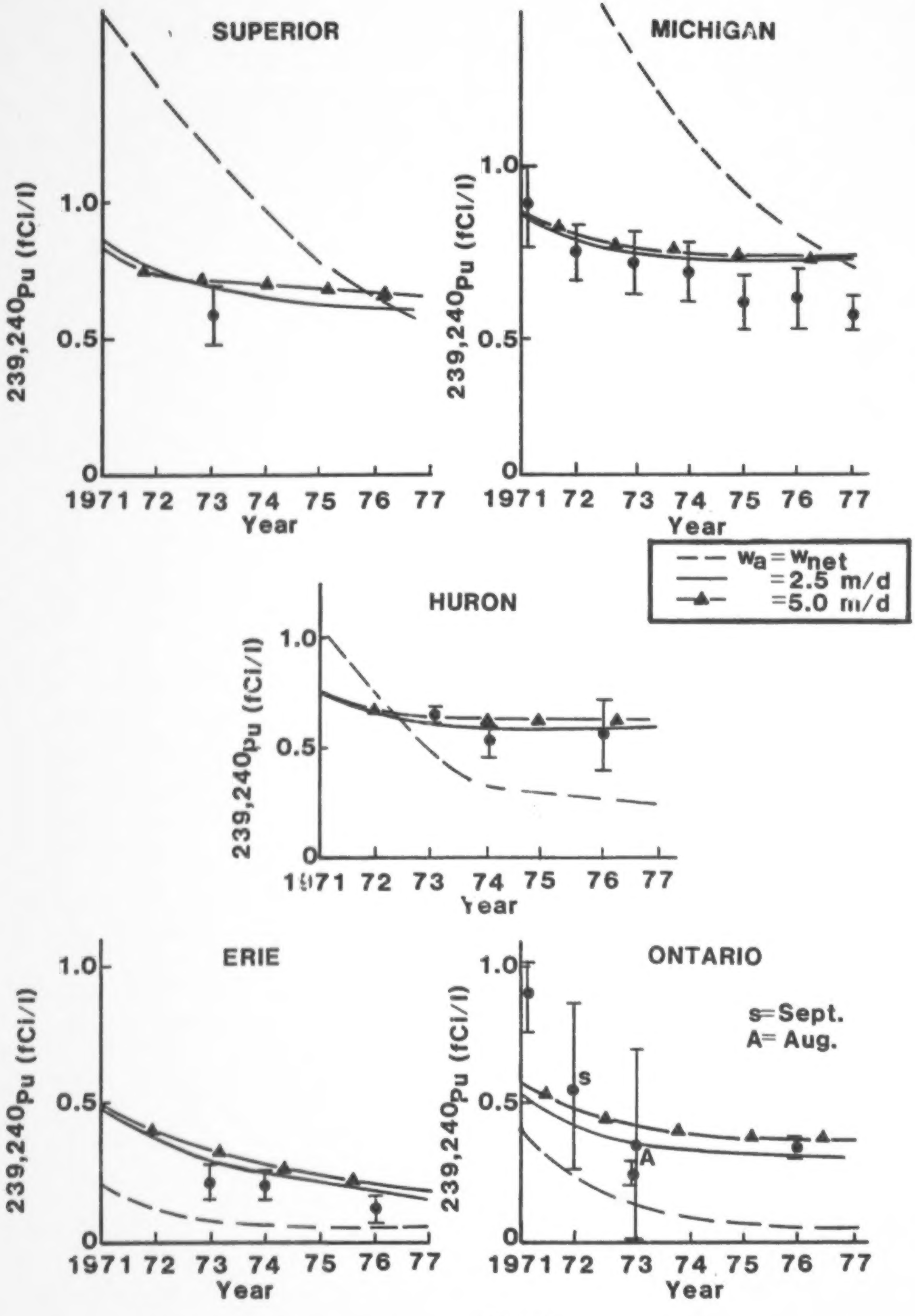
The data available for calibration in the water column have been compiled by Wahlgren, et al., (1981). For all lakes, data were obtained beginning in 1971, i.e. towards the end of the loading time history shown in Figure 24. In the sediments, data on plutonium concentration with depth have been reported for Lake Michigan by Edgington, et al., (1975).

The calibration procedure described above was then applied to the fully time variable equations for the period 1953-1977 beginning with zero plutonium concentration everywhere. Figure 25 shows the full time history calculated for Lake Michigan under three conditions in the settling velocity and for a partition coefficient of 400,000 ℓ/kg. Since the available data began only in 1971, particular interest centers around the latter years where the data can be better compared to the dynamic calculation. Figure 26 shows the results for the five lakes for 1971-1977 and the conditions of settling velocity. When attention is focused more directly on these latter years, the calibration is clearly not favorable for $w_a = w_n$, i.e. resuspension equal to zero. For Lakes Superior and Michigan, this case results in concentrations that are substantially higher than the observed data due to the low loss rate from the water column. For the other lakes however,the no resuspension case underestimates the data. At a settling rate of 2.5 m/d, and associated resuspension the results are much more favorable. The increase in settling to 5 m/d with increased resuspension does not result in any substantial change in the calculation in these later years since under both cases the sediment as the primary driving force has reached an equilibrium that is independent of the sediment interactions. Sensitivity analyses also indicated that increasing the partition coefficient to 1,000,000 ℓ/kg and considering zero resuspension ($w_a = w_n$) does not adequately reproduce the data. The increased partition coefficient does result in lowered water column concentration but the dynamic behavior is not representative of the data shown in Figure 26.

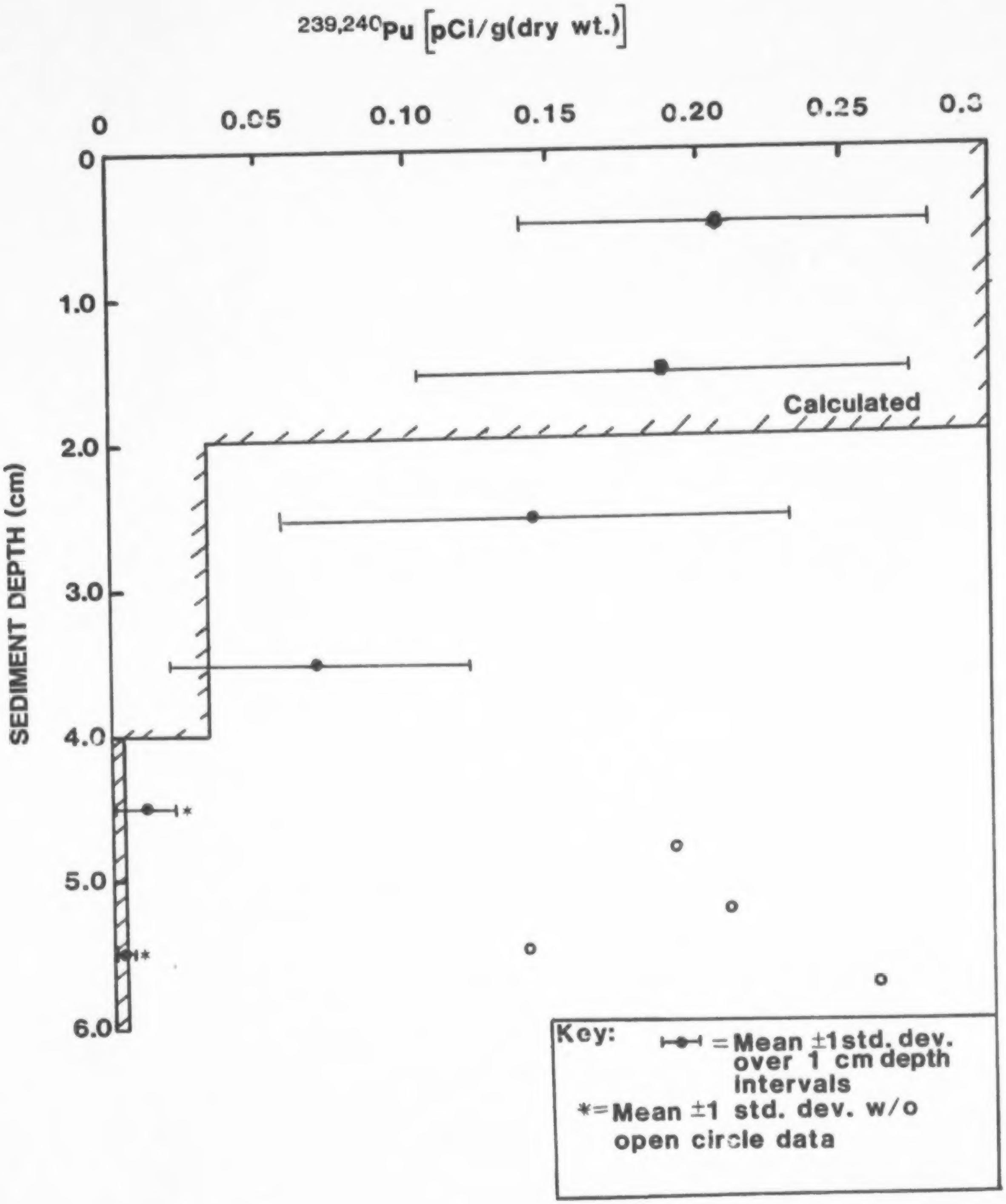
Figure 27 shows the calibration to the plutonium sediment data for Lake Michigan in 1973-1974 reported by Edgington, et al. (1975). The sediment concentration as calculated approximately reproduces the observed data. The introduction of sediment mixing (as for example due to bioturbation) would smooth the sediment calculation to more adequately reflect the observed data. Also it should be noted that the observed data are for areas of net deposition while the calculation is for a lakewide sediment average. The comparison then implies that the model overestimated the mass of plutonium in the sediment. It may be hypothesized, however, that the nondepositional areas of the lake do not have zero concentration but may include a layer of particulate matter of unknown thickness but at the approximate concentrations shown in Figure 27. (Edgington, et al., 1975 discuss this possibility and the reported plutonium concentrations of surface sediment floc are similar to the surface values shown in Figure 27.) The remaining mass of plutonium that was not observed is then hypothesized to be contained in this layer of particulate matter in the nondepositional zones.



25. Comparison of calculated Lake Michigan ^{239,240}Pu concentration (fC_i/ℓo in the water column to 1971-1977 data for three conditions of the particulate settling velocity. π = 400,000 ℓ/kg, (Data from Wahlgren, et al., 1981).



26. Comparison of calculated ^{239,240}Pu concentration (fC$_i$/ℓ) in the water column for all lakes to 1971-1977 data for three conditions of the particulate settling velocity. π = 400,000 ℓ/kg. (Data from Wahlgren, et al., 1981).



27. Comparison of calculated ^{239,240}Pu concentration (pC$_i$/g(d)) in the sediment of Lake Michigan to observed data for 1973-1974. w_a = 2.5 m/d, π = 400,000 ℓ/kg. (Data from Edington, et al., 1975).

Figure 28 shows the calculated time history of the particulate plutonium concentration in the water column and surface sediment of Lake Michigan and Central Lake Erie. The concentration calculated for Lake Michigan in the mid-1970's of 0.27 $pC_i/g(d)$ is at the upper end of the range of values reported by Wahlgren and Marshall (1975) of 0.13 to 0.26 $pC_i/g(d)$. This may be due to an overestimation of the effective partition coefficient. A similar comment applies to the overestimation in the surface sediment. The calculation indicates that the water column and sediment particulate plutonium concentration for Lake Michigan are not in equilibrium due to the small net solids deposition velocity. On the otherhand, for a region such as Central Lake Erie (Fig. 28 (b)), the particulate concentrations are calculated to be in equilibrium because of the more responsive coupling of sediment and water column as a result of higher net depositional velocities. The substantially lower particulate concentration for Lake Erie is coupled to a lower dissolved concentration resulting from the increased solids concentrations in that basin.

The relevant time variable response for the sediment is given approximately from a simplified version of Eqs. (22 and 23), i.e.

$$\frac{dc}{dt} = \frac{W}{V} - \frac{c}{t_o} - \frac{w_a}{H_1} f_p c + \frac{w_{rs}}{H_1} f_{ps} c_s \tag{73}$$

$$\frac{dc_s}{dt} = \frac{w_a f_p c}{H_s} - \frac{w_{rs}}{H_s} f_{ps} c_s - \frac{w_s}{H_s} f_{ps} c_s \tag{74}$$

If resuspension is neglected, i.e. $w_a = w_{net}$, then the sediment does not interact with the water column and the two equations are decoupled. An approximate response time can then be readily calculated. The solution for the sediment equation for a constant input beginning at time t=0 from the water column is:

$$c_s = \frac{w_a f_p c}{w_s} (1-\exp-(\frac{w_s}{H_s}) f_{ps} t)_s \tag{75}$$

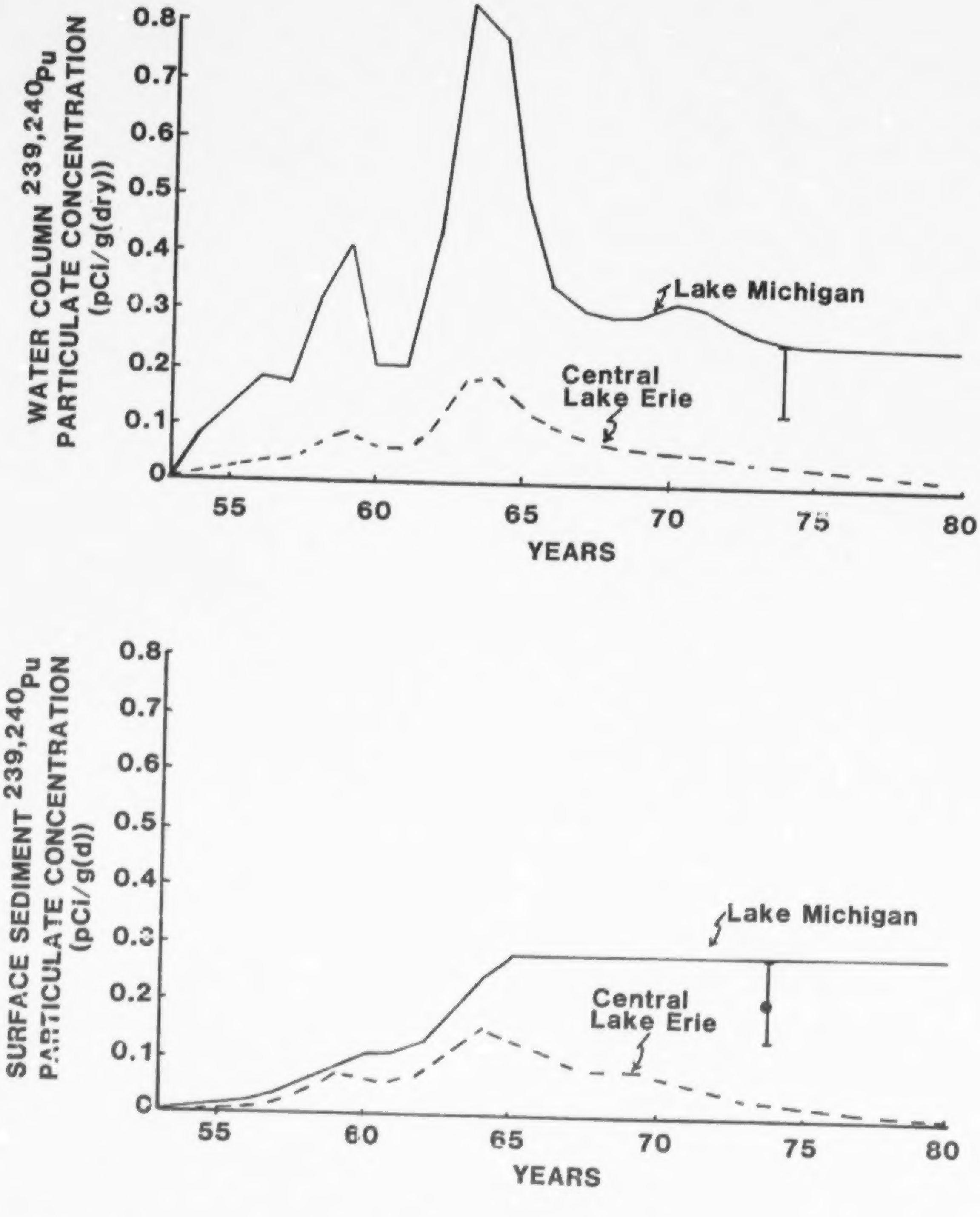
Similarly, the water column is

$$c = \frac{W/V}{1/t_o + w_a f_p/H} (1 - \exp(-(1/t_o + w_a f_p/H))t) \tag{76}$$

So that for the sediment, the approximate time to respond to one half of an equilibrium level from an input from the water column is:

$$(t_{1/2})_{sed.} = \frac{0.69}{(\frac{w_s}{H_s}) f_{ps}} \tag{77}$$

and for the water column is:



28. Calculated time history of particulate plutonium concentration (µg/g(d) in (a) water column (vertical bar in 1974 is range reported by Wahlgren and Marshall, 1975) and (b) surface sediment for Lake Michigan and Central Lake Erie (data shown in 1979 is mean ± standard deviation for Lake Michigan from Edington, et al., 1975.

$$(t_{1/2})_{water} = \frac{0.69}{\frac{1}{t_o} + \frac{w_a f_p}{H}} \qquad (78)$$

Table 13 shows the approximate response times for the two cases of Lakes Michigan and Erie. As seen, the sediment response time is about an order of magnitude greater than the response time of the water column for both lakes. For Lake Erie, however, the response time of both the water column and the sediment is about an order of magnitude lower than that of Lake Michigan. This is due to several factors associated with Lake Erie: a) the more shallow depth, b) the higher fraction of ^{239}Pu in the particulate form, and c) the higher net sedimentation velocity.

The sediment for a lake, such as Lake Michigan, therefore, is estimated to respond with a time frame of tens of years to external load changes whereas for a more shallow lake, such as Lake Erie, the surface sediment might be expected to track the water column concentration. An equilibrium calculation using the fugacity concept of Mackay and Paterson (1981) or of Eadie, et al (1981) between water column and sediment would not result in a response similar to that shown in Figure 16. For example, in the latter calculation, the water column and sediment are assumed to be always in equilibrium with each other and, therefore, the sediment concentration behaves in a similar manner to the water column. The calculation shown in Figure 28 and as the simple equations (77) and (78) and Table 13 show, an equilibrium assumption for a well-mixed sediment layer of 2 cm for Lake Michigan may not be a good one. Of course, one could argue that the assumption of a well-mixed layer is not valid and that the sediment-water interface is always in equilibrium. In this model, however, the well mixed assumption appears to be reasonable in the light of the data. Nevertheless, the dynamic relationships between the sediment and the water column is sensitive to the assumption of the depth of the well-mixed sediment layer.

Table 14 shows the magnitude of the resuspension velocities for each of the Lakes or regions and the ratio of the resuspension velocity to the sedimentation velocity. Figure 29 shows this ratio as a function of the particulate settling velocity. These results are calculated from Eq. (72) with the net loss of solids and sedimentation rates given from Table 10. As seen, for the range of settling velocity from 2.5-5.0 m/d, the resuspension velocity is about 2-10 times the net sedimentation velocity for the upper lakes and about 10-20 times the net sedimentation velocity for Western Lake Erie. Saginaw Bay, a more shallow body of water (see Table 7) involves a high degree of turnover of internal solids where the ratio of resuspension to sedimentation velocities is on the order of 100-200. This presumably reflects the larger impact of wind induced resuspension. The lowest ratio of w_{rs} to w_s is for Lake Ontario.

Figure 30 shows the fluxes of plutonium for year 20 (1973) in Lake Michigan under the three conditions on the particulate settling velocity.

TABLE 13

COMPARISON OF APPROXIMATE RESPONSE TIMES FOR ^{239}PU IN WATER COLUMN AND SEDIMENT OF LAKES MICHIGAN AND ERIE

($w_a = w_{net}$; No resuspension)

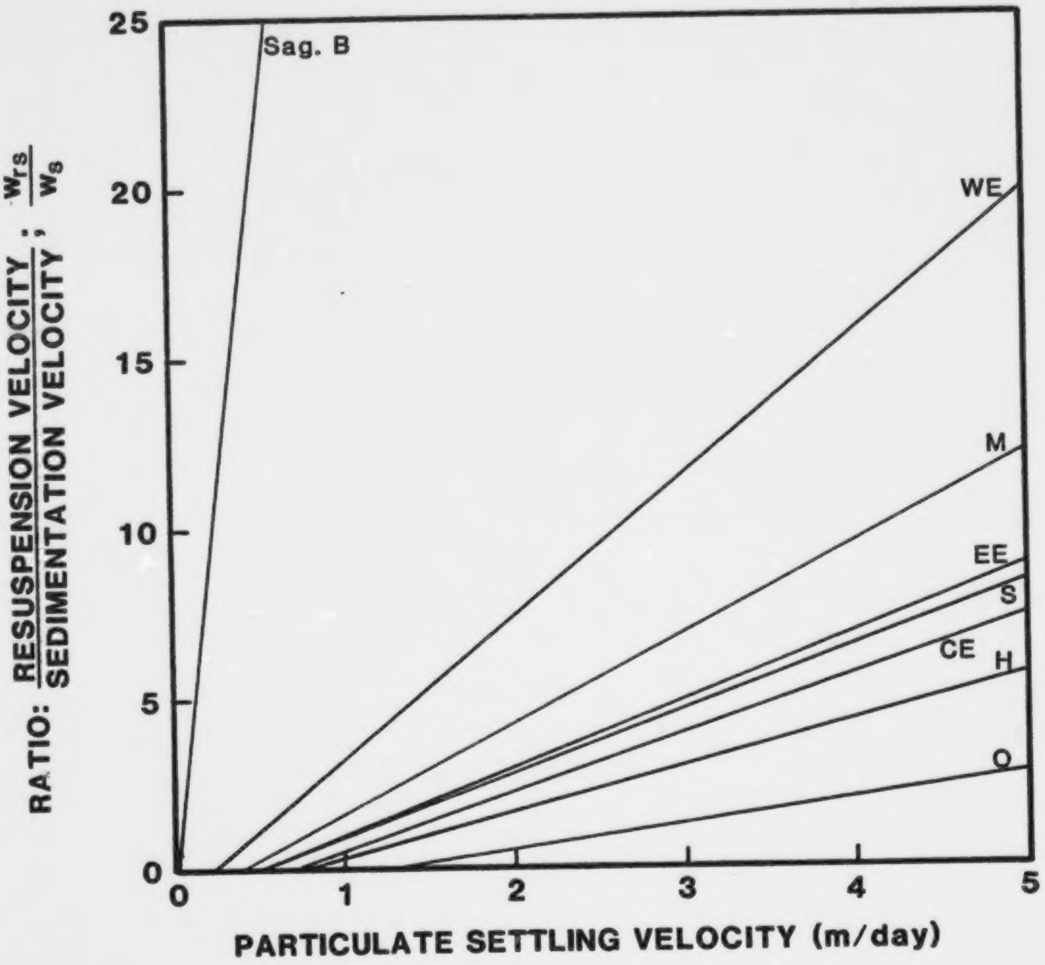
	Water Column					Sediment		
	Det. Time (t_o) yr.	Depth (H_1) m	Sett. Vel (w_a) m/yr	Fract. Part.[1] (f_{po})	50% Response Time($t_{½}$) (yr)	Depth (H_2) cm	Sedim. Vel. (w_s) mm/yr	50% Response Time ($t_{½}$) yr
Lake Michigan	100	90	137	0.17	2.6	2.0	0.3	46.0
Lake Erie	2.9	20	200	0.67	0.1	2.0	4.0	3.4

[1] @ π = 400,000 $pC_i/kg \div pC_i/\ell$; Michigan @ 0.5 mg/ℓ; Erie @ 5 mg/ℓ

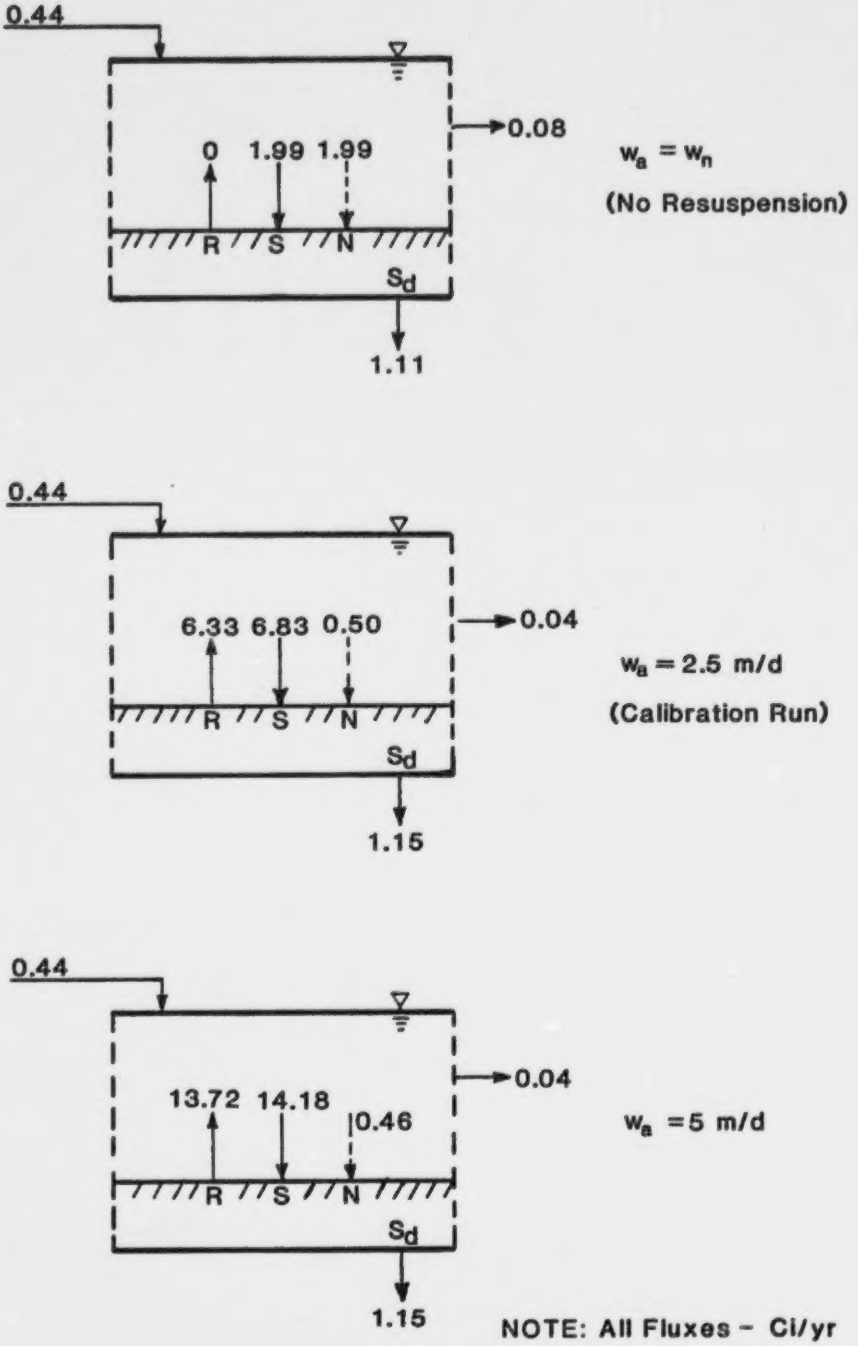
TABLE 14

RESUSPENSION VELOCITIES FOR DIFFERENT PARTICULATE SETTLING VELOCITIES

Lake or Region	w_{rs}=Resuspension Velocity (mm/yr) for w_a=Particulate Settling Velocity of		w_s=Sed. Vel. mm/yr	Ratio w_{rs}/w_s
	2.5 m/day	5.0 m/day		
Superior	1.51	3.43	0.41	3.7- 8.4
Michigan	1.64	3.58	0.29	5.6- 12.3
Huron	1.35	3.26	0.56	2.4- 5.8
Saginaw Bay	30.53	61.33	0.27	113.1-227.1
Western Lake Erie	68.80	144.85	7.25	9.5- 20.0
Central Lake Erie	14.50	33.50	4.50	3.2- 7.4
Eastern Lake Erie	11.20	25.25	2.85	3.9- 8.9
Ontario	0.89	2.80	1.02	0.9- 2.7



29. Ratio of resuspension velocity to sedimentation velocity as a function of particulate settling velocity.


0.44
0.08
0
1.99
1.99
R
S
N
S_d
1.11
$w_a = w_n$
(No Resuspension)
0.44
0.04
6.33
6.83
0.50
R
S
N
S_d
1.15
$w_a = 2.5$ m/d
(Calibration Run)
0.44
0.04
13.72
14.18
0.46
R
S
N
S_d
1.15
$w_a = 5$ m/d

NOTE: All Fluxes - Ci/yr

R = Resuspension Flux
S = Settling Flux
S_d = Sedimentation Flux
N = Net Flux to Sediment

30. Calculated plutonium flux for Lake Michigan in year 20 under different particulate settling velocities.

The outflow from the Lake is relatively small and represents only about 10% of the incoming load. For all cases, net loss to the deep sediment is virtually independent of particulate settling and reflects the 20 year loading of the sediment. Also, the net input of plutonium to the sediment is not affected by the particulate settling velocity since the resuspension flux increases by a factor of two to compensate for the doubling of the settling velocity.

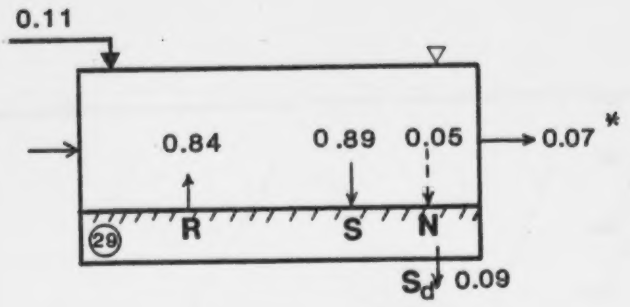
Figure 31 shows the calculated plutonium flux for the three basins of Lake Erie for year 20 and the calibration settling velocity of 2.5 m/d. It is seen that the water column for each basin is in approximate equilibrium. The surface sediment, however, is not in equilibrium at year 20 for each of the basins reflecting the sediment detention times of abut 3 years, 4 years, and 7 years for the western central, and eastern basins respectively. Thus, the surface sediment is still fluxing to the deeper sediment the plutonium flux from the earlier higher loading to the lake system. Also, in terms of total flux (and areal flux), the surface sedimentation loss to the deeper sediment is highest for the central basin of Lake Erie.

Additional Sensitivity Calculations

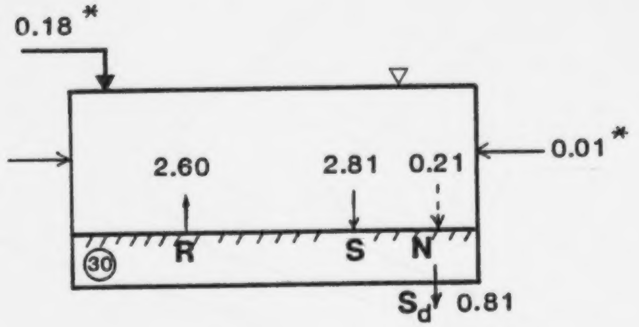
The sensitivity of the plutonium calculation was also examined through other model calculations where in addition to varying the settling and resulting resuspension velocities as in the calibration analysis, and the partition coefficient was varied to evaluate the sensitivity of the calculation.

Figure 32 shows the sensitivity of the plutonium water column concentration in Lake Michigan to the partition coefficient for the case of zero resuspension, i.e. $w_a = w_{net}$. The objective of this calculation was to determine whether an increased partition coefficient with no resuspension would equally well represent the observed data. Although the concentration at $\pi = 1{,}000{,}000$ ℓ/kg is approximately equal to the data, the dynamic response indicates that it undershoots the data by 1973-1974. In general, increasing the partition coefficient decreases the water column concentration as shown and therefore the water concentration is sensitive to a one order magnitude increase in the partition coefficient even at the solids level of 0.5 mg/ℓ. In the sediment of Lake Michigan, however, the sensitivity is not as marked as shown in Table 15.

The surface sediment concentration (0-2 cm) as noted varies from 0.22 to 0.31 for an approximate order of magnitude increase in partition coefficient for the no resuspension case ($w_a = w_{net}$). This range is within the range of data as shown in Figure 27. Also, for the fixed partition coefficient, the variation in sediment concentration as calculated by the model is not sensitive to the settling and resuspension condition that was assigned. These results indicate that the sediment plutonium data in a large lake such as Lake Michigan is not sensitive enough to distinguish between settling and resuspension characteristics. However, the approximate 30% change in calculated particulate concentration as a result of the approximate one order of magnitude change in partition co-

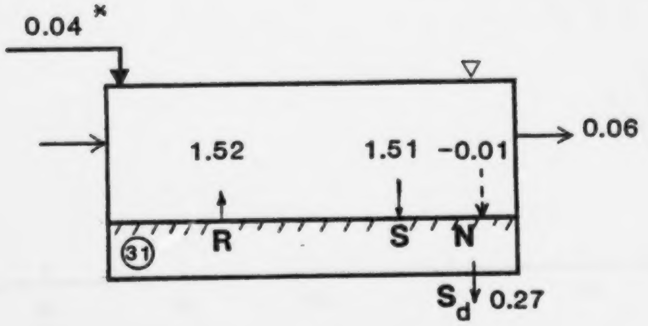

0.11
0.84
0.89
0.05
0.07 *
29
R
S
N
Sd 0.09

LAKE ERIE WESTERN BASIN


0.18 *
2.60
2.81
0.21
0.01 *
30
R
S
N
Sd 0.81

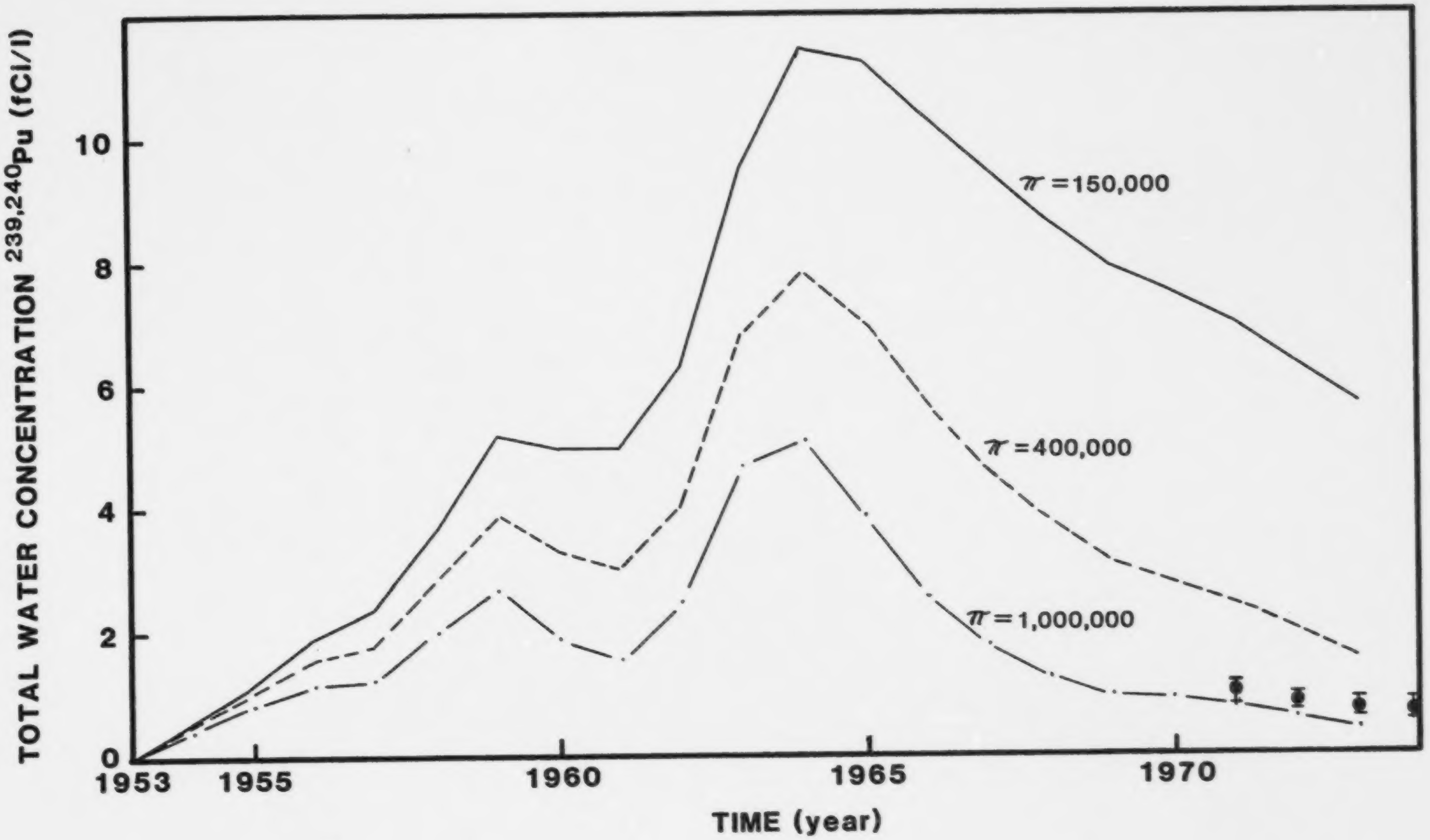
LAKE ERIE CENTRAL BASIN

NOTE: ALL UNITS- C_i/yr
R=RESUSPENSION FLUX
S= SETTLING FLUX
N= NET FLUX TO SEDIMENT
S_d= SEDIMENTATION FLUX
* - INCLUDES HORIZONTAL EXCHANGE FLUX


0.04 *
1.52
1.51
-0.01
0.06
31
R
S
N
Sd 0.27

LAKE ERIE EASTERN BASIN

31. Calculated plutonium flux for Western Central and Eastern Lake Erie in year 20; w_a = 2.5 m/d.



32. Sensitivity of water column plutonium concentrations to partition coefficient; $w_a = w_{net}$.

TABLE 15
SENSITIVITY OF PLUTONIUM SEDIMENT CONCENTRATION TO SETTLING VELOCITY AND PARTITION COEFFICIENT - LAKES MICHIGAN AND ERIE, 1973 CALCULATED VALUES

Lake Michigan

	Calculated Sediment $^{239,240}Pu$ Conc. (pC_i/g)		
	0-2 cm	2-4 cm	4-6 cm
π = 150,000 ℓ/kg) $w_a = w_{net}$	.22	.017	.0007
π=1,000,000(ℓ/kg) $w_a = w_{net}$	.31	.030	.0014
π = 400,000(ℓ/kg) $w_a = w_{net}$	.29	.25	.0011
w_a = 2.5 m/d	.30	.033	.0017
w_a = 5.0 m/d	.30	.033	.0017

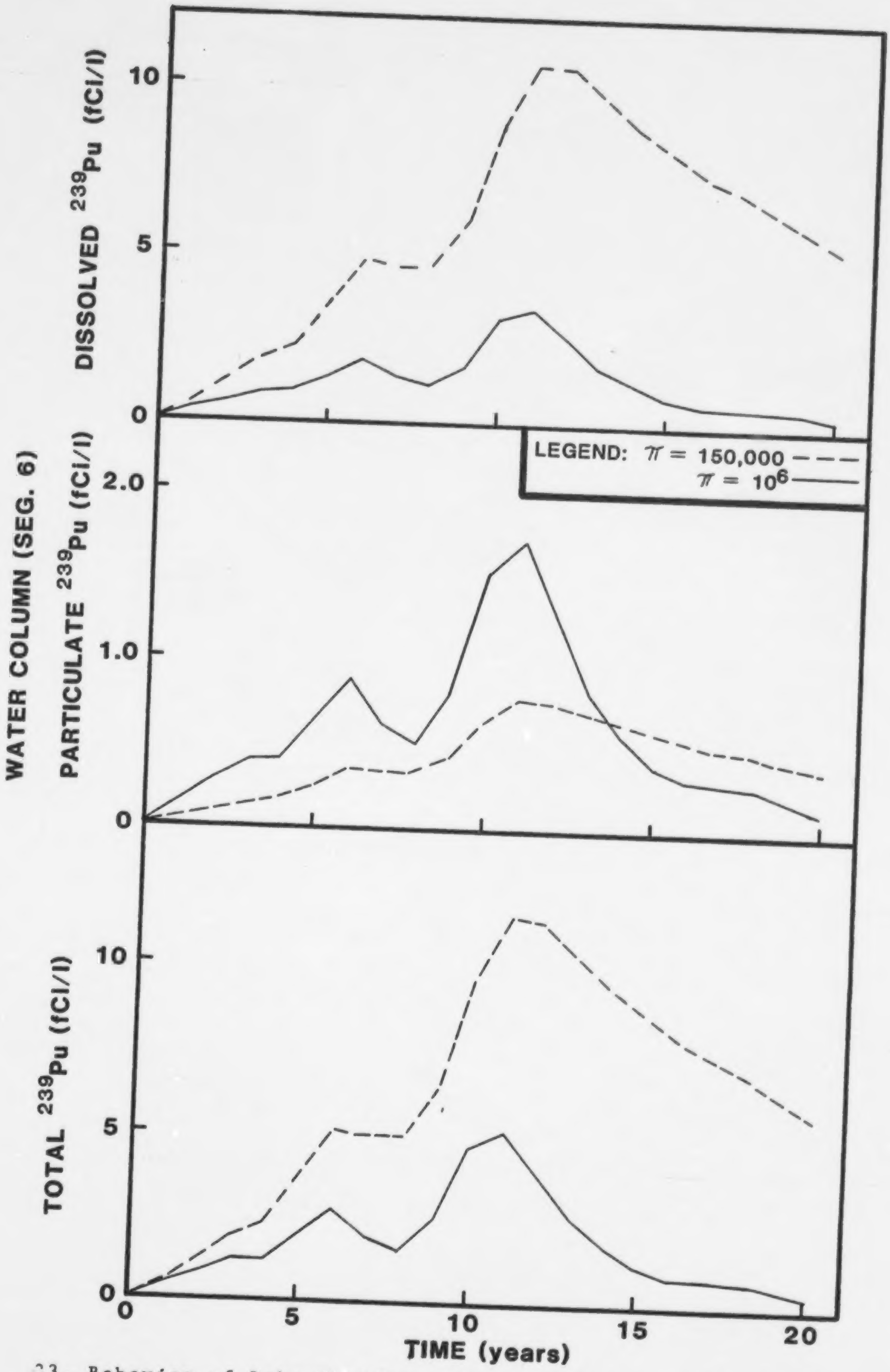
Lake Erie

	Calculated Sediment $^{239,240}Pu$ Conc. (pC_i/g)								
	0-2 cm			2-4 cm			4-6 cm		
	West	Cent.	East	West	Cent.	East	West	Cent.	East
π = 150,000 ℓ/kg $w_a = w_{net}$	.059	.063	.078	.091	.095	.084	.094	.075	.044
π = 1,000,000 ℓ/kg $w_a = w_{net}$	.016	.045	.060	.036	.078	.074	.046	.066	.044
π = 400,000 ℓ/kg $w_a = w_{net}$	.026	.049	.053	.051	.082	.080	.062	.068	.058
w_a = 2.5 m/d	.018	.046	.053	.031	.077	.074	.040	.064	.044
w_a = 5.0 m/d	.017	.046	.053	.030	.076	.073	.038	.064	.044

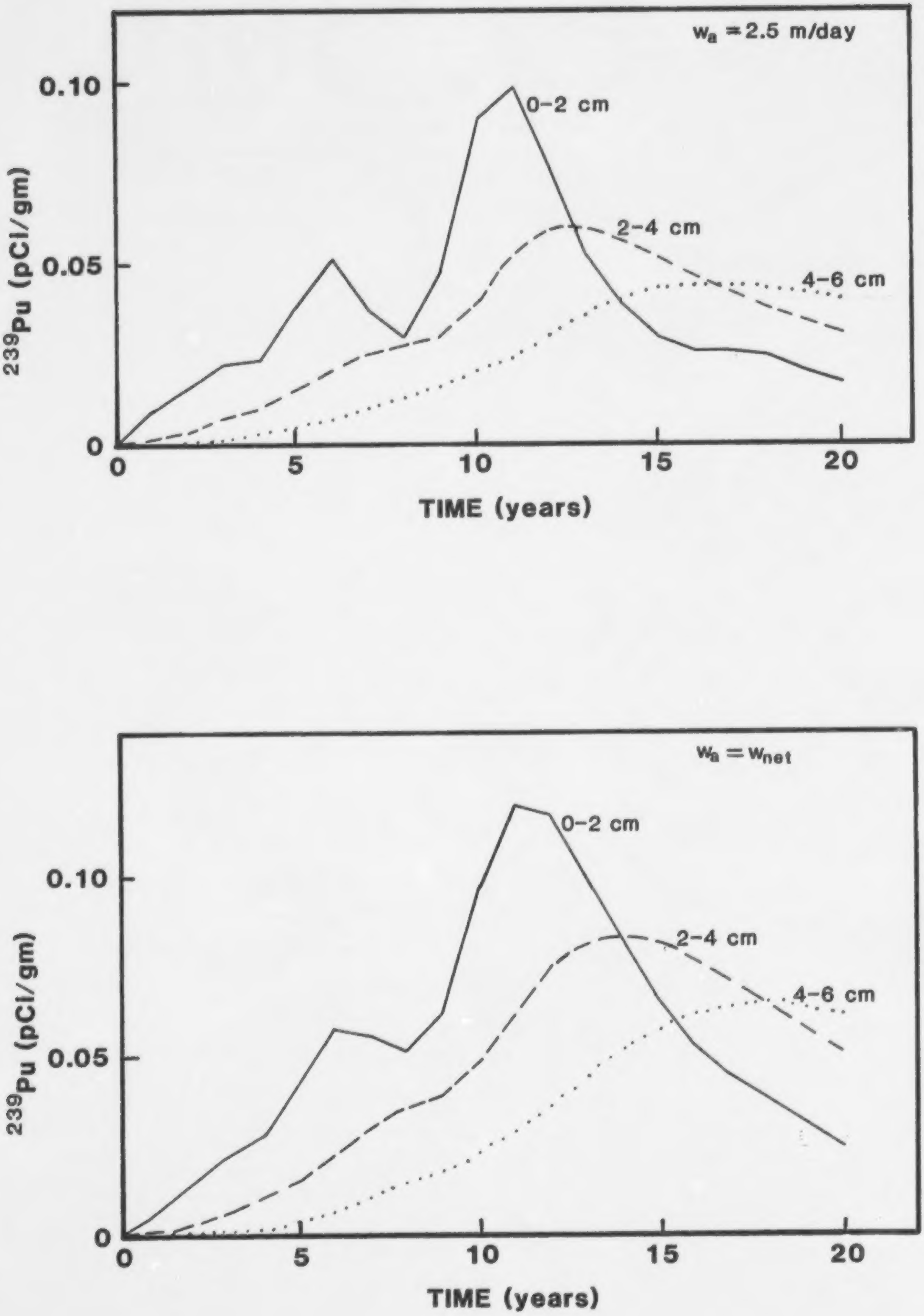
efficient may prove useful in calibration of sediment data with variable partition coefficient.

Figure 33 shows the dynamic behavior of the plutonium water column concentration under the two conditions on partition coefficient, again for the case of zero resuspension. The upper panel indicates the behavior of the dissolved fraction which varies as might be expected, i.e. increasing the partition coefficient sorbs more plutonium on to the solids and therefore reduces the dissolved concentration. As seen in the lower panel, the effect of increasing partition is to increase the net loss out of the water column and thereby reduce the total. The middle panel, however, shows a rather peculiar behavior in the particulate form. This form of plutonium is increased with increasing partitioning until abut year 14 where a cross-over occurs and the particulate plutonium under the higher partitioning is less than that under the lower partitioning. This appears to be due to the overall net loss of total plutonium for the higher partitioning and resulting reduced dissolved plutonium to sorb onto the particulates.

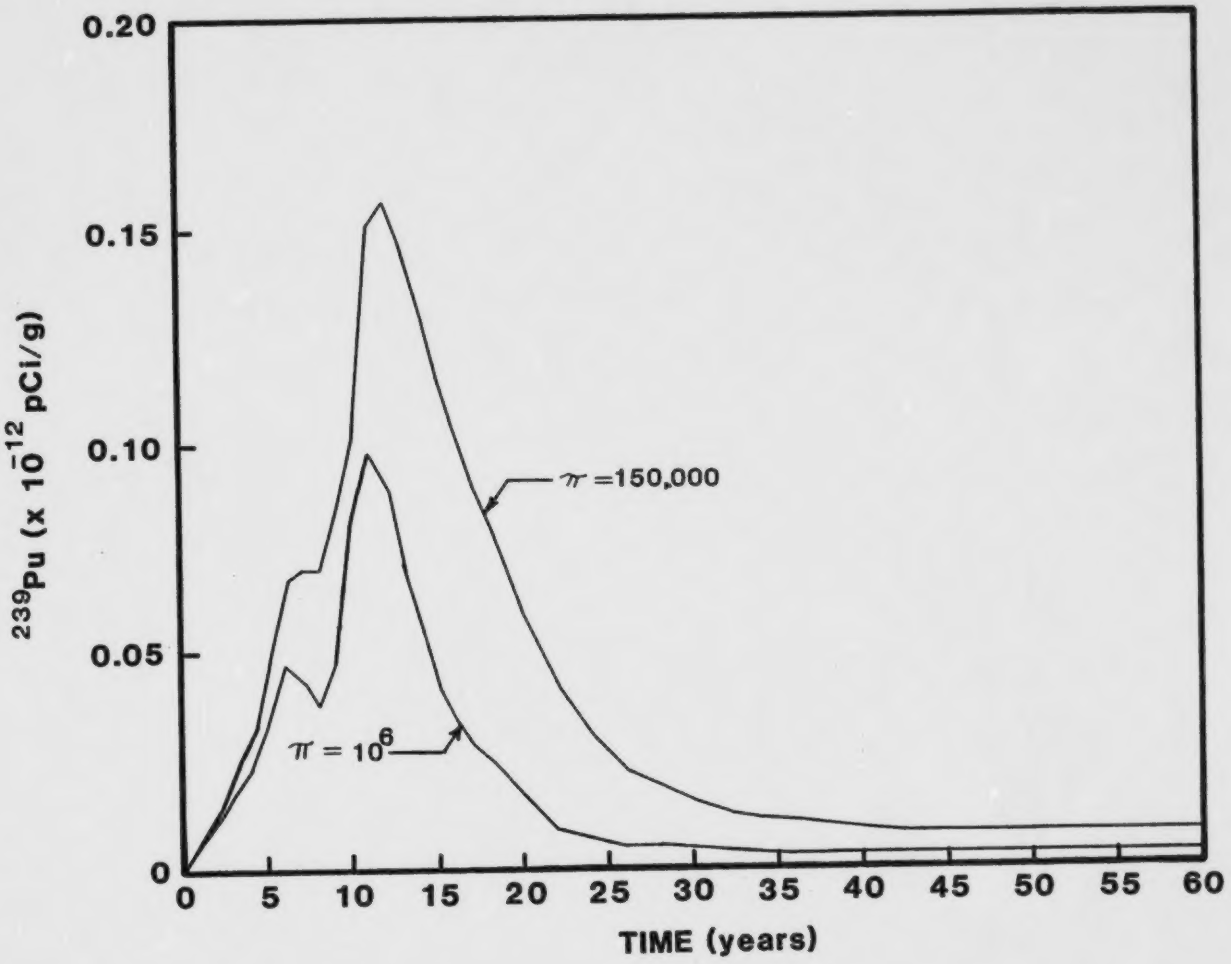
Table 15 also show the sensitivity of the calculated plutonium sediment concentration for Lake Erie. As indicated, for a fixed partition coefficient of 400,000 ℓ/kg, the more interactive Western Basin sediment is sensitive to the settling and resuspension characteristics whereas the Central and Eastern Basins are not. Resuspension in the Western Basin reduced the surface sediment plutonium concentration by about 30%. The penetration into the sediment of the Western Basin is illustrated in Figure 34 where again the sensitivity to including resuspension is not marked. Also, the calculations shown in Table 15 are interesting since they indicate that for 1973, the higher partition coefficient of 1,000,000 ℓ/kg resulted in the lowest concentration in the sediment in almost all basins and sediment depths. One would have expected (as in Lake Michigan) that increasing the partition coefficient would sorb more plutonium onto the sediment solids whereas the opposite effect is calculated for Lake Erie. This appears to be due to the dynamic, nonsteady state nature of the loading to a system such as Lake Erie. Continuing the calculation under a constant loading would according to the steady state theory result in a return of surface sediment concentrations at a lower level with lower partition coefficient. Figure 35 shows, however, that this is not the case since for an additional 40 years of constant loading (year 20-60), the surface plutonium concentration at the higher partion coefficient is still less than at the lower partition coefficient. The only explanation for this behavior is that the response of the Western Basin is still a nonsteady state response and that the relatively simple behavior of the steady state model is not always appropriate. This appears to be the case especially when it is recognized that the detention time of the surface 2 cm sediment of Lake Huron is about 36 years and for Lake Michigan about 69 years. Figure 33 already displayed the rather anamolous behavior of the particulate form for Lake Michigan and since Western Lake Erie is responding to the long term response of the upper Lakes, one can not readily apply the simple reasoning of the steady state model to the time variable nature of the entire system.



23. Behavior of Lake Michigan plutonium water column concentration under two partition coefficients; $w_a = w_{net}$.



34. Calculated sediment plutonium concentration for Western Basin, Lake Erie; π = 400,000 ℓ/kg.



35. Long term calculation of plutonium concentration in surface sediment of Western Lake Erie for two partition coefficients, w_a = 2.5 m/d.

Conclusions

The following conclusions may be drawn from the calibration of the model to the $^{239,240}Pu$ data and the associated sensitivity analyses.

(1) Particulate settling velocity of 2.5 m/d to 5 m/d with resulting resuspension velocity to maintain a solids balance is operative throughout the Lakes. The resuspension velocity should be viewed as a parameter of the model representing the complex interaction of near shore resuspension, horizontal transport and deposition and open lake resuspension and transport. Chambers and Eadie (1981) in their work on particulate matter in Lake Michigan report transient resuspension phenomena vertically and horizontally that tend to result in large scale resuspension of particulates.

(2) The result of the inclusion of the resuspension phenomena is to retain concentrations of plutonium in the water column over longer periods of time than would occur without the mechanism. This appears to be consistent with the observed data.

(3) The calibration to the observed sediment data in Lake Michigan indicates that some sediment mixing between the 2 cm layers may be occurring as a result of mechanisms such as bioturbation.

(4) The sensitivity analyses indicate that the dynamic behavior of the water column concentration of plutonium is most sensitive to variations in settling and resuspension velocities, and partition coefficients. The 0-2 cm sediment plutonium concentrations do not vary significantly as a function of settling and resuspension characteristics or partition coefficient indicating that data over the 0-2 cm depth is not a sensitive calibrating data set for use in determining model parameters of settling and resuspension.

(5) The time variable calculations result in system behavior of a chemical such as plutonium that is different than the steady state. For example, the calculations indicate that the particulate plutonium decreases with increasing partition coefficient for certain Lakes (e.g. Western Lake Erie).

SECTION 8
PCB MODEL OF GREAT LAKES

The analysis of suspended solids and ^{239,240}Pu can also be applied to calculate PCB levels in the Lakes as an example of the model framework utility. However, there is a great deal of difficulty in calculating a mass balance for PCBs in the Great Lakes in spite of the preceding analyses. This is due to a) uncertainty in input loads, b) uncertainty in the significance of certain PCB mechanisms such as volatilization, and c) a wide range of reported levels of PCB in the water column. The calculation of PCB in the water column and sediment is, at best, therefore an order magnitude calculation and, therefore, quite dissimilar to the ^{239,240}Pu results discussed previously.

CONTEMPORARY EXTERNAL PCB LOADS

In these calculations, estimates are made of the contemporary PCB input loads (i.e. approximately within the past 5-10 years). A complete load history of PCB input over the past 30 years for the Great Lakes system is not available at the present time.

The principal external sources of PCB to the Great Lakes are:

a) atmospheric input from precipitation and dry deposition,
2) tributary inputs representing up-basin discharges of PCB and subsequent transport to the Lakes,
3) direct inputs of municipal and industrial PCB loads to the Lakes.

Atmospheric Input

The concentration of PCB in precipitation over the Great Lakes has been determined by Murphy and Rzeszutko (1978) and Strachan and Hunealt (1979). These results and the data reported by Wells and Johnstone (1978) are summarized in Table 16.

As seen, the mean concentrations differ by almost a factor of five which may reflect sampling or analytical variations. (The reported concentration for the East Coast of Scotland is included for reference.) Strachan and Hunealt (1979) reported significantly different levels for the various stations located in the Lake's basins, i.e. mean values of 26 ng/ℓ for Superior, 11 ng/ℓ for Huron, 9 ng/ℓ for Erie, and 32 ng/ℓ for Ontario. Because of the variability in reported values of PCB precipitation concentration, a range of 10-100 ng/ℓ was chosen for an input load estimate.

Dry deposition has been estimated by Eisenreich, et al. (1979) for Lake Superior. In their estimate, 10% of the measured PCB air concentrations (range 0.1-10 ng/m^3) was assumed to be in the particulate form and a deposition velocity of 0.005 m/s was used. The input of PCB to Lake Superior then from dry deposition was estimated at $0.1 \cdot 10^3$ to $1 \cdot 10^3$ kg which for a surface area of $8.21 \cdot 10^{10}$ m^2 is an areal loading of from 0.12 to $1.2 \cdot 10^{-5}$ g PCB/m^2-yr. This range in the areal

TABLE 16
SOME REPORTED CONCENTRATIONS OF PCB IN PRECIPITATION

Location	Concentration (ng/ℓ)		Reference
	Mean	Std. Dev.	
Lake Michigan (35 samples)	111		(1)
Lakes Superior, Huron, Erie, and Ontario	21	30	(2)
East Coast Scotland	15	-	(3)

(1) Murphy and Rzeszutko (1978)
(2) Strachan and Huneult (1979)
(3) Wells and Johnstone (1978)

TABLE 17

ESTIMATED RANGE OF CONTEMPORARY TOTAL PCB LOADING (kg/yr)

Lake	Atmos-pheric[a]	Tribu-tary[b]	Mun. & Ind.[c]	Total	Atmospheric Load as % of Total
Superior	60-7550	630-1890	5- 60	1390-9500	28-92
Michigan	530-5310	460-1380	70- 700	1060-7390	20-91
Huron	310-3080	410-1510	5- 80	730-4670	16-88
Saginaw Bay	30- 330	270- 530	5- 50	310- 910	5-55
Erie-West	30- 280	100- 300	160-1620	290-2200	2-52
-Central	140-1450	80- 220	40- 450	260-2120	17-92
-East	60- 580	60- 160	10- 100	130- 840	19-89
Ontario	180-1830	330- 990	130-1260	640-4080	7-80

(a) Atmospheric loading range: precipitation, 10-100 ng/l; dry deposition, $1\cdot2\cdot10^{-6}$ to $1\cdot2\cdot10^{-5}$ g/m^2-yr.

(b) Tributary loading @ 10-30 ng/l, except Saginaw Bay where tributary input data were directly available.

(c) Mun. & Ind. direct point source loading @ 0.1-1.0 ug/l @ municipal direct point source flows.

deposition rate was used for each of the segments in the model. Table 17 presents the atmospheric input loading ranges (precipitation plus dry deposition) for each of the Great Lakes and regions.

Tributary Input

Konasewich, et al. (1978) have summarized a variety of isolated data on concentration of PCB in tributaries to the Great Lakes and that work together with work on the Saginaw River and the Canadian rivers is summarized in Table 18. The range is quite large for any given tributary and reflects transient events associated with suspended solids resuspension, probable differences in analytical techniques throughout the Great Lakes region and, of course, variable point and non-point source loadings to the tributaries. In view of the range in the data and the difficulty of determining, in detail, the effect of each upon basin loading, it was decided to assign a range of concentration from 10-30 ng/ℓ to the tributary flows into each Lake or region. The resulting range of tributary loading by segment and for the Lakes as a whole is shown in Tables 17.

Municipal and Industrial Input

Data on the concentration of PCBs in municipal and industrial point sources throughout the Great Lakes have been summarized by Konasewich, et al. (1978). Again, the range of reported concentrations is wide (from about 0.1-100 ug/ℓ). Also, Mueller and Anderson (1978) in a survey of data on PCB in municipal plants (including Canadian plants in the Great Lakes basin) reported a range in average concentration from <0.2-1.2 ug/ℓ. Given the range in reported concentrations, and the unavailability of any detailed reliable data base on individual point source inputs directly to the Lakes (as opposed to the tributary inputs which include up-basin point sources), a range of concentration of PCB from 0.1-1.0 ng/ℓ was used.

This range was applied to the estimated municipal point source discharge flows directly entering the model segments and the totals are shown in Table 17.

PCB MASS BALANCE

As noted in Table 17, the range in the total input PCB loads is consequently estimated to be about a factor of 5-8 from lowest to highest estimates depending on assumptions made regarding PCB levels in precipitation and loading due to other sources, such as tributary, municipal, and industrial inputs. Also, the time history of all of the PCB inputs is not known with certainty. Accordingly, in this computation, the inputs are held steady at the two levels shown in Table 17 and the results therefore are reflective of a range of concentrations for a range of input loads.

The partition coefficient was assumed at 100,000 ℓ/kg (Di Toro, et al., 1982a; Richardson, et al., 1983; Thomann, 1981) throughout the Lakes. As indicated by both Di Toro, et al., (1982a) and Eadie, et al. (1983), the PCB partition coefficient may be a function of the solids

TABLE 18

SOME REPORTED PCB CONCENTRATIONS IN GREAT LAKES TRIBUTARIES

Lake or Region	Total Water ng/l	PCB Conc. on Susp. Solids ng/g	Remarks	Reference[(a)]
SUPERIOR	27		Calc. from reported trib. load of 1740 kg/yr.	(1) p. 215
		20 (10- 30)	Mean and range of Canadian tribs. (1975)	(2) p. 75
MICHIGAN				
Platte R.	15		Aroclor 1254	(1) p. 289
HURON				
Cheboygan R.	500			(1) p. 164
Saginaw R.	74		1979 mean and range	(3)
		84 (20- 370)	Mean and range of Canadian tribs. (1974)	(2) p. 75
		20 (8- 30)	Mean and range of Canadian tribs. (1975)	(2) p. 75
ERIE		60 (10- 330)	Mean and range of Canadian tribs. (1975)	(2) p. 75
Grand R.	2.6±.65		Mean ± 95% limits, 9 samples, (1976)	(1) p. 39
Cuyahaga R.	39 -589		1973 data	(1) p. 28
Tribs. to Cuyahaga R.	48 -482		1973 data	(1) p. 28
Agricult. Plots	38 ND-110		1975-1976 data	(1) p. 35
	25		1976-1977 data	(1) p. 35
ONTARIO		194 (2-1800)	Mean and range of Canadian tribs. (1974)	(2) p. 75
Oakville Cr.	3.5±1.2		Mean± 95% limits, 9 samples, (1976)	(1) p. 39

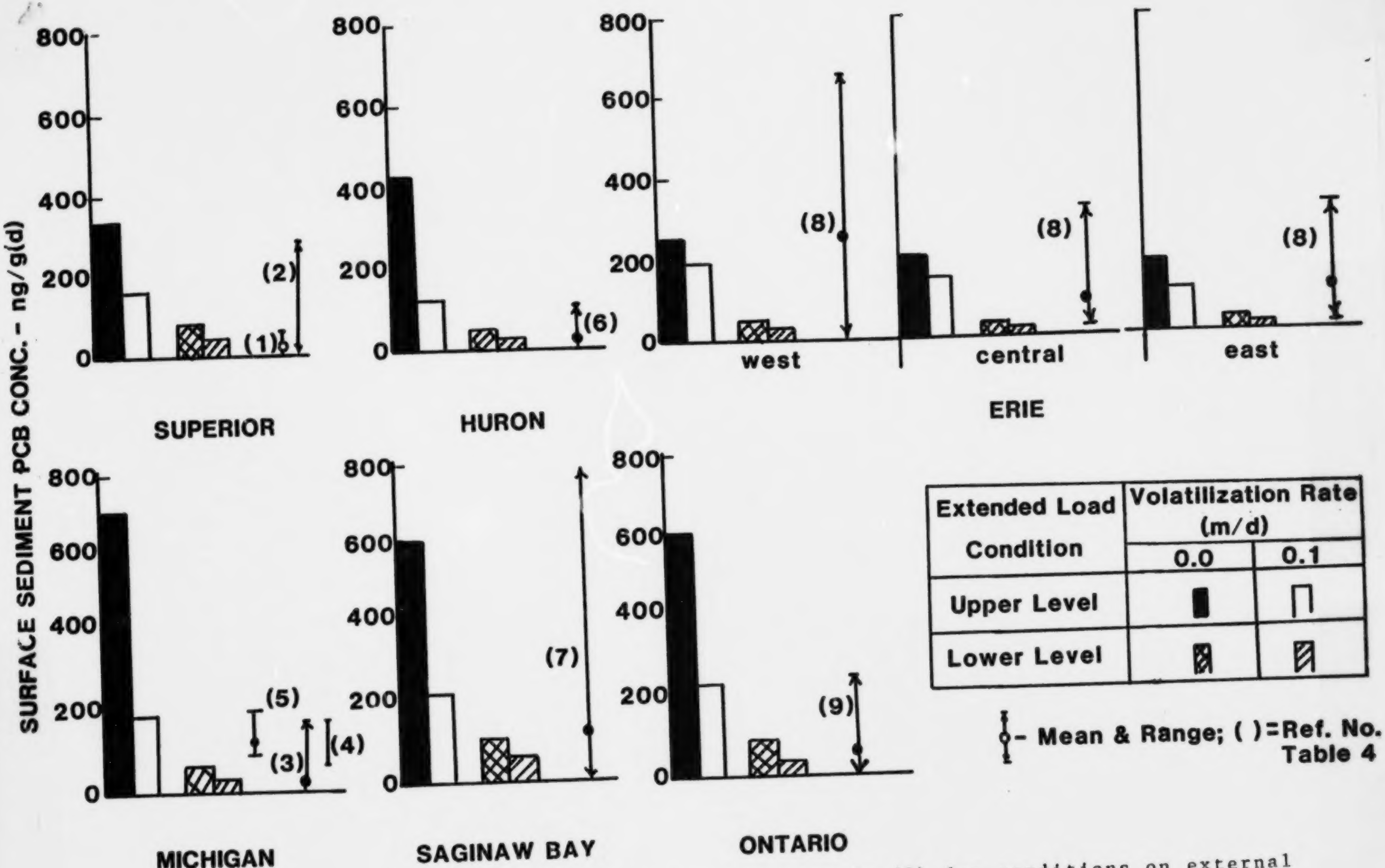
(a) (1) Konasewich, et al. (1978)
(2) Frank (1977)
(3) U.S. EPA Grosse Ile Laboratory

concentration and at the high solids concentration in the sediment may decrease by one to two orders of magnitude or more. The sensitivity of the calculation to a solids dependent partition coefficient is discussed in Section 10.

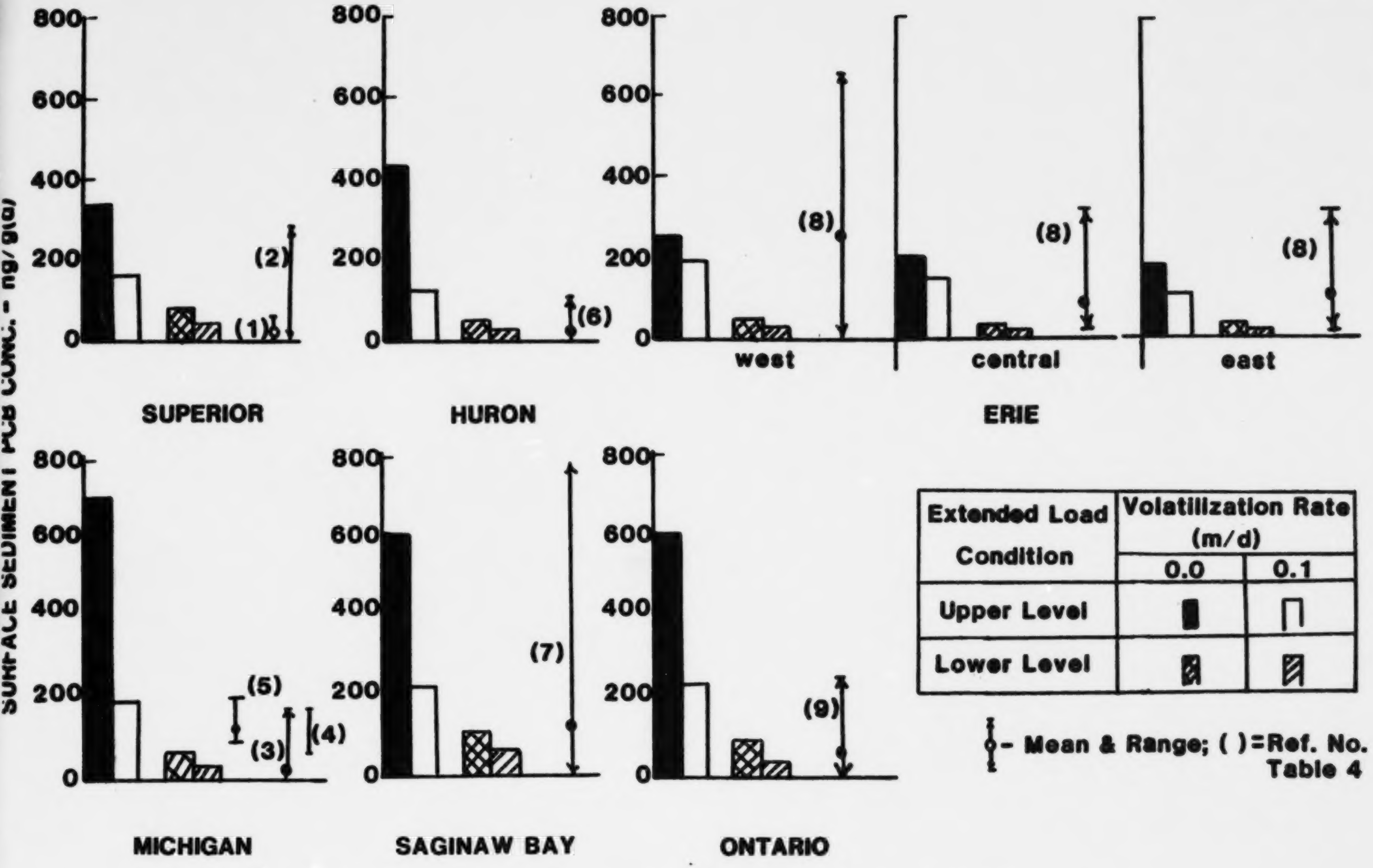
The PCB volatilization transfer rate for PCB was estimated using the general approach of O'Connor (1982). A Henry's constant of 0.114 mm Hg/mg/ℓ and a 5 m/s wind were used from which the liquid film coefficient is 0.11 m/d and the gas film coefficient of 71.4 m/d can be calculated using 1254 PCB. The lake-atmosphere exchange process is then liquid film controlled and for this work an overall exchange rate of 0.1 m/d was used. In order to show the effect on the calculation of volatilization at this rate, a zero exchange was also used.

The results of the four conditions (high and low load levels, with and without volatilization) after running the preceding calibrated model for 20 years to an approximate steady state are shown in Figures 36 and 37. Zero initial conditions were assumed throughout. The water column calculations shown in Figure 37 can be compared to only a few contemporary measurements of PCB concentration. Past reported data have often fluctuated by an order of magnitude. For example, results for Lake Ontario were reported in 1972 at 55 ng/ℓ (Haile et al., 1972) but were later questioned by Veith (1976a, 1976b) who indicated that the actual value may be only on the order of several ng/ℓ. For Lake Superior, Swain (1978) reported values for open waters (in 1974-1976) at 5 ng/ℓ, Eisenreich, et al (1983) reported lakewide average levels of 1.3 ng/ℓ (1978), 3.6 ng/ℓ (1979), and 0.9 ng/ℓ (1980), and Rice, et al. (1982) reported values in the range of 1-11 ng/ℓ for 1979-1980 in Lake Michigan. The model results shown in Figure 36 range from 3 to 9 ng/ℓ for the upper load level without volatilization of 0.25 to 0.5 ng/ℓ for the lower load level with volatilization. Comparison to the very limited water column data indicates that the upper load level without volatilization overestimates the data in the open lake waters. The effect of volatilization of PCB as indicated in Figure 36 is to reduce the steady state water column concentration by 50-70% except for Lake Erie where the reduction due to volatilization is about 30%. This reflects the higher fraction of PCB in the particulate phase for Lake Erie due to the higher solids concentration. THe inclusion of volatilization also has a significant effect on the time to reach equilibrium. For example, for Lake Michigan at the upper level of loading without volatilization, the time to equilibrium in the water column is greater than 20 years in contrast to less than 10 years when volatilization is included.

The comparison to sediment PCB data as shown in Figure 37 is complicated by different years of sampling of the surface sediment. Table 19 lists the reported PCB surface sediment concentrations and as noted, the sampling dates vary from 1968 for Lake Ontario to 1978-1980 for Saginaw Bay. To order of magnitude, the reported data are in the range from 10-100 ng/g(d) with some indication of higher concentrations in lower lakes although as noted the reported data for Lakes Erie and Ontario are for 1971 and 1968 and may be reflecting higher loadings



36. Calculated water column total PCB concentration (ng/ℓ) for conditions on external load (see Table 17) and volatilization rate.



37. Calculated surface sediment PCB concentration (ng/g) for conditions on external load (see Table 17) and volatilization rate and comparison to observed data (see Table 19).

TABLE 19
SOME REPORTED PCB SURFACE SEDIMENT CONCENTRATIONS (ng/g)

Lake	Mean	Std.Dev.	Range	No. of Samples	Year	Remarks	Ref.
Superior	3.3	5.7	<2.5- 57	405	1973	0-3 cm	(1)
			5-290		1977	0-0.5 cm	(2)
Michigan	9.7	15.7	< 2-190	286	1975	0-3 cm	(3)
			64-160	3	1980	0-1 cm	(4)
	132	48	91-201	5	-	0-1.5 cm	(5)
Huron	13	-	3- 90	174	1969	0-3 cm	(6)
Sag. Bay	118	-	2-968	59	1978-80		(7)
Erie							
-West	252	156	4-660	24	1971	0-3 cm	(8)
-Central	74	56	12-330	71	1971	0-3 cm	
-East	86	85	12-320	29	1971	0-3 cm	
Ontario	57	56	< 5-280	229	1968	0-3 cm	(9)

Ref. (1) Frank, et al. (1980)
(2) Eisenreich, et al. (1979)
(3) Frank, et al. (1981)
(4) Eadie, et al. (1981)
(5) Armstrong and Swackhamer (1983)
(6) Frank, et al. (1979a)
(7) Richardson (Private Communication)
(8) Frank, et al. (1977)
(9) Frank, et al. (1979b)

prior to or during that period. As shown in Figure 37, the upper load level without volatilization overestimates the reported values in all Lakes except Erie. Better agreement to observed sediment data is obtained at the other conditions. From the comparison to water and sediment data then, the upper level without volatilization is not considered to be a representative condition. For Lakes Superior, Michigan and Huron, the lower level of loading with volatilization represents the observed data more adequately than other conditions.

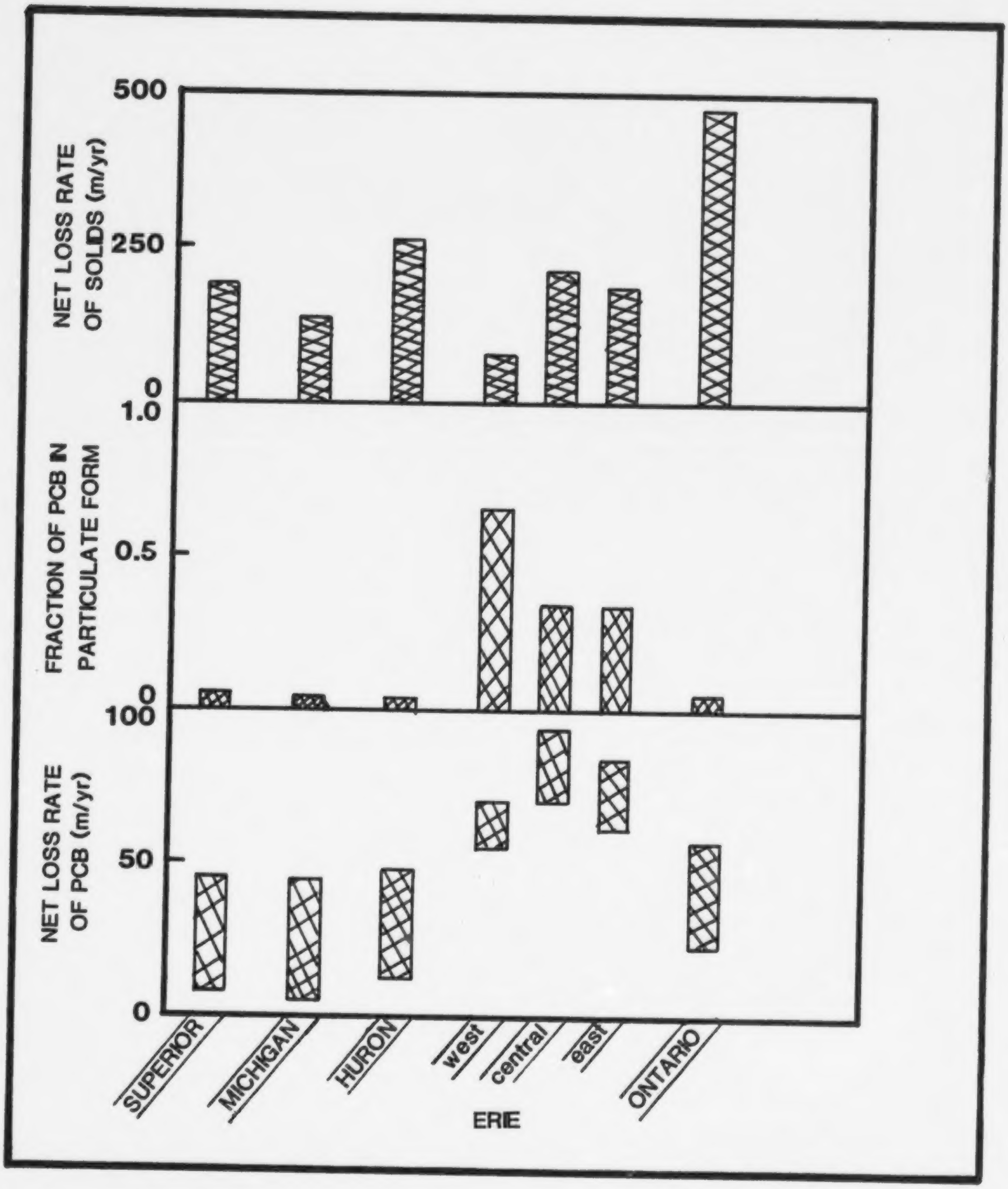
As with the water column, the calculated time to equilibrium in the sediment is markedly influenced by volatilization. For Lake Michigan, the sediment does not reach equilibrium even after 20 years without volatilization but approaches equilibrium within 20 years with volatilization. In contrast, western Lake Erie is calculated to reach equilibrium with volatilization in about 10 years. The observed 0-3 cm data shown in Figure 37 and Table 19 therefore represent a long term integration of previous load inputs and the calculations using the calibrated model indicate that the range of conditions on loading and volatilization encompasses to order of magnitude the previous load history. The comparison of calculated PCB sediment concentrations to observed PCB data tends to indicate that volatilization may be a significant mechanism although the data do not permit a definitive conclusion. The model results do indicate that if the range of present loading continues, the water column and sediment concentrations shown in Figure 37 can be expected to continue.

Discussion

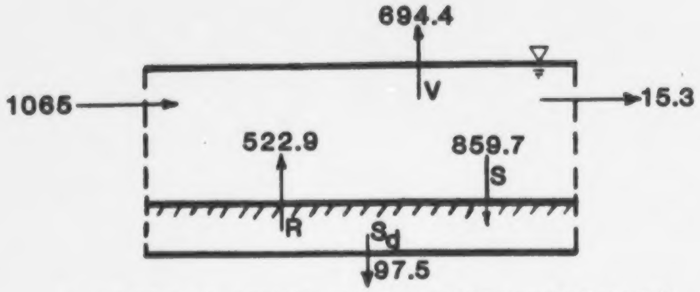
The effect of the higher solids concentrations in Lake Erie is seen in Figure 38 where the net loss of PCB (as estimated from Eq. 63) is significantly higher for that Lake. Eq. 63 indicates that the higher fraction particulate for Lake Erie coupled with the net deposition of solids results in a higher net loss rate of PCB from the water column. Further, since the fraction particulate for Lake Erie is relatively high, the resulting dissolved concentration will tend to be lower, providing at least a partial explanation for the lower levels of PCB in the fish of Lake Erie.

The mass balance of PCB as calculated from the model after 20 years of steady input is shown for Lakes Michigan and Erie in Figures 39 and 40. Volatilization is included.

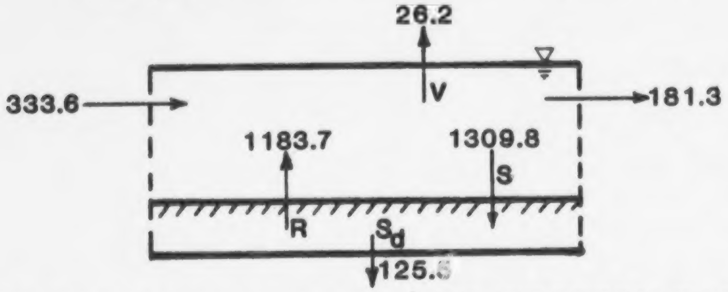
For Lake Michigan, it is seen that the downstream transport of PCB is small (about 1% of the input) indicating that the PCB load remains in the Lake and enters the sediment via net deposition. Resuspension flux of PCB is about 50% of the incoming load and net deposition is about 30% of the incoming load. About 65% of the incoming load is lost due to volatilization. Also for Lake Michigan, the water column is in approximate equilibrium but the sediment is not although the flux difference results in a small change in sediment concentration so that for practical purposes, the sediment can be considered at approximate equilibrium (see also Fig. 28).



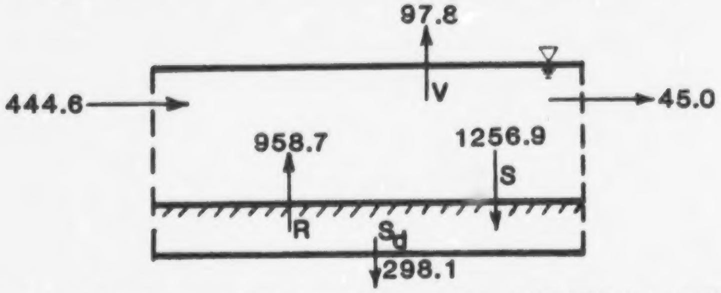
38. Relationship between net loss of solids (top), fraction of PCB in particulate form (middle) and range of net loss of PCB (bottom), calculated from Ea. 63.


694.4
V
1065
15.3
522.9
859.7
S
R
S_d
97.5

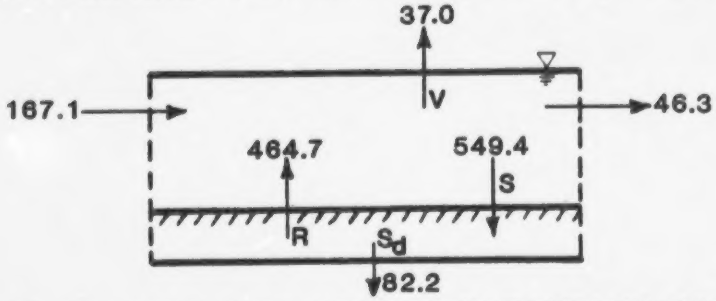
MASS BALANCE FOR LAKE MICHIGAN


26.2
V
333.6
181.3
1183.7
1309.8
S
R
S_d
125.5

MASS BALANCE FOR LAKE ERIE WESTERN BASIN


97.8
V
444.6
45.0
958.7
1256.9
S
R
S_d
298.1

MASS BALANCE FOR LAKE ERIE CENTRAL BASIN

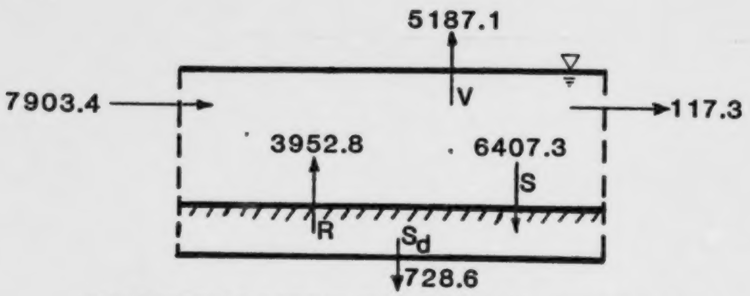

37.0
V
167.1
46.3
464.7
549.4
S
R
S_d
82.2

MASS BALANCE FOR LAKE ERIE EASTERN BASIN

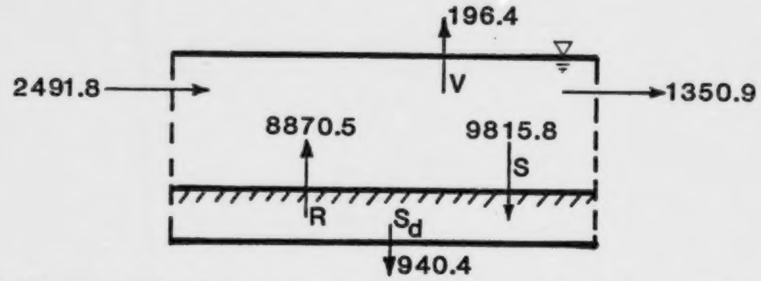
NOTE: All Fluxes – kg/yr

R = Resuspension Flux
S = Settling Flux
S_d = Sedimentation Flux
V = Volatilization Flux
N = Net Flux to Sediment

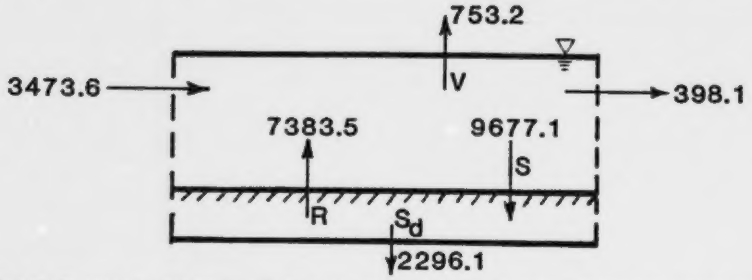
39. Mass balance of PCBs, Lakes Michigan and Erie after 20 years of steady input of low level of PCB load.


5187.1
V
7903.4
117.3
3952.8
6407.3
S
R
Sd
728.6

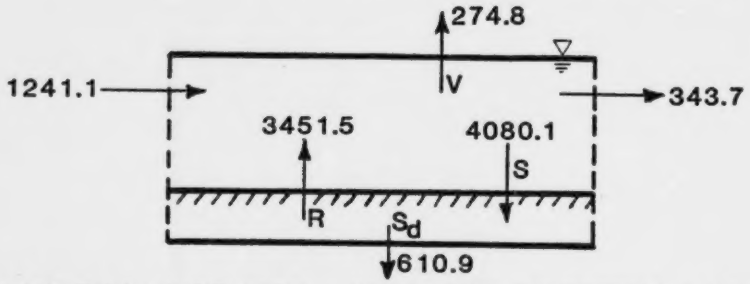
MASS BALANCE FOR LAKE MICHIGAN


196.4
V
2491.8
1350.9
8870.5
9815.8
S
R
Sd
940.4

MASS BALANCE FOR LAKE ERIE WESTERN BASIN


753.2
V
3473.6
398.1
7383.5
9677.1
S
R
Sd
2296.1

MASS BALANCE FOR LAKE ERIE CENTRAL BASIN


274.8
V
1241.1
343.7
3451.5
4080.1
S
R
Sd
610.9

MASS BALANCE FOR LAKE ERIE EASTERN BASIN

NOTE: All Fluxes – kg/yr

R = Resuspension Flux
S = Settling Flux
S_d = Sedimentation Flux
V = Volatilization Flux
N = Net Flux to Sediment

40. Mass balance of PCBs, Lakes Michigan and Erie, after 20 years of steady input of high level of PCB load.

In contrast to Lake Michigan, Lake Erie in all basins and for both water column and sediment has reached an approximate equilibrium during the 20 year calculation period. As noted previously, (see Eqs. 77 and 78 and Table 13), the rapid equilibrium for Lake Erie is due to the more shallow depth and the higher sedimentation velocity for that Lake. Also, in contrast to Lake Michigan, the advective and dispersive transport out of the Western Basin in particular is about 50% of the incoming load with only 8% being lost to volatilization (versus 65% for Lake Michigan). The lower flux due to volatilization is a function of the higher solids concentration in the Western Basin and the resulting lower concentration of dissolved PCB available for exchange to the atmosphere. Also, in contrast to plutonium, the Western Basin of Lake Erie receives the highest areal flux of PCB of the three basins of the Lake (42-312 g PCB/km^2-yr). The resulting sediment PCB concentration, however, does not differ markedly from the other basins because of the higher sedimentation velocity for the Western Basin. This can be seen from Eq. (51) where

$$c_{Ts} = \frac{W_{net}/A}{w_s} \tag{79}$$

where W_{net}/A is the net areal flux of PCB delivered to the sediment. As indicated in Table 10, the sedimentation velocity for the Western Basin is higher than the other two basins resulting in a difference in PCB sediment concentrations of about 35%. This difference is less than the difference in observed sediment concentrations between the Western Basin and the Central and Eastern Basins as shown in Table 19. The observed mean surface sediment concentration of 252 ng/g in the Western Basin in 1971 may reflect a higher loading to the basin during that time.

Conclusions

It is concluded from the application of the plutonium calibrated model to PCBs in the Great Lakes that:

a) the estimated upper level of present PCB loading (ranging from 4080 kg/yr for Lake Ontario to 9500 kg/yr for Lake Superior) without volatilization is probably too high,

b) from the available data, it is not possible, at the present time, to distinguish the appropriate combination of loading and loss due to volatilization,

c) lower levels of PCB in Lake Erie are probably due to the higher net loss of PCB from elevated solids concentrations and resulting fraction of PCB in the particulate form.

d) the response time for Lake Michigan to equilibrate to a steady PCB load with volatilization is less than 20 years for the water column but greater than 20 years for the sediment.

e) the Western Basin of Lake Erie delivers the highest net flux of PCB to the sediment of the three basins of the Lake.

f) volatilization of PCB is significant for Lake Michigan (about 65% of incoming load) but is less significant for Lake Erie (about 8%) due to the higher solids concentration in that lake.

SECTION 9
PLUTONIUM AND PCB RESPONSE TIMES

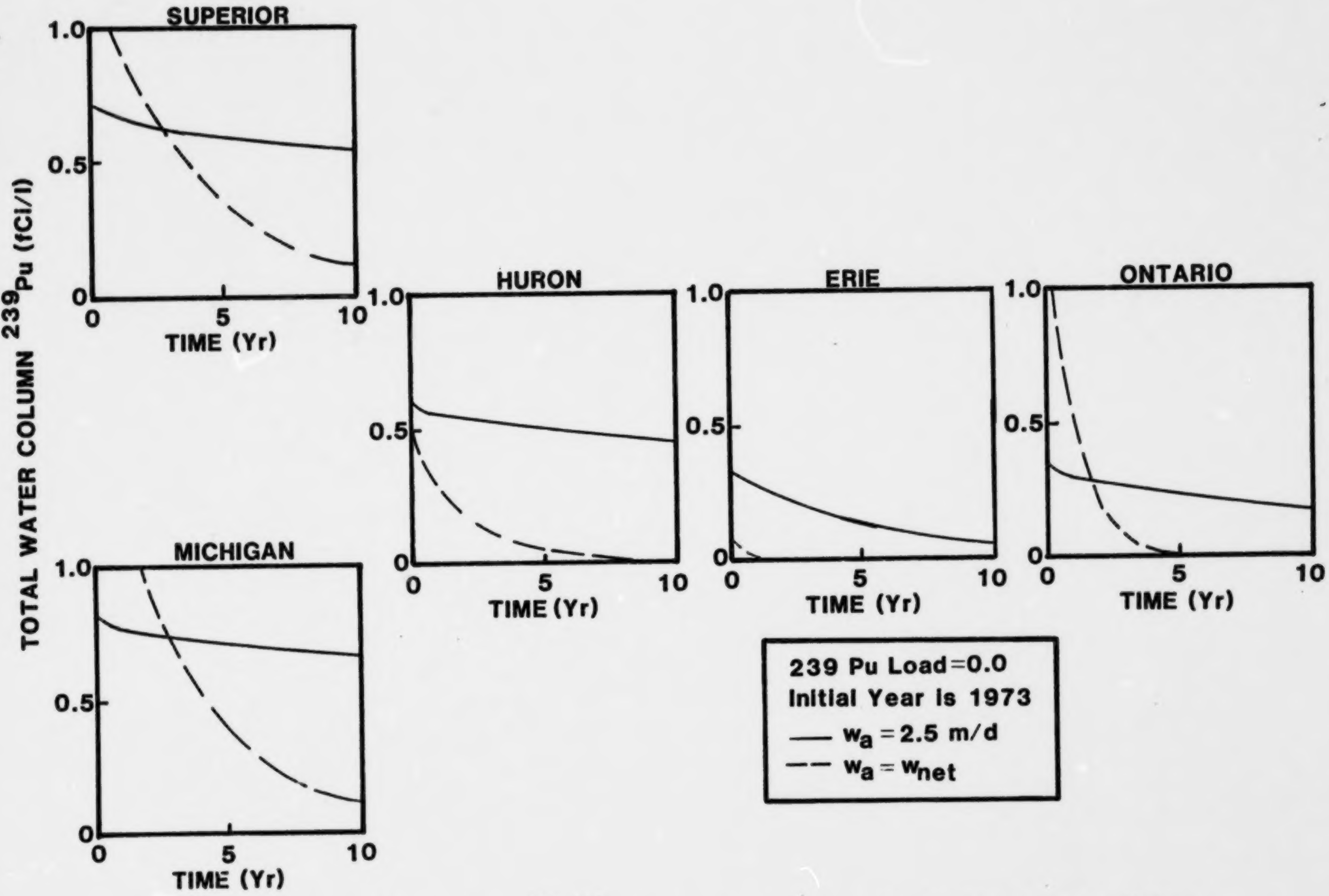
PLUTONIUM

The response time of the toxic substance model applied in this research has been analyzed by Di Toro, et al. (1981) who indicate that the response is composed of two parts following a load decrease: a rather rapid reduction in the water column due to initial water column-sediment equilibration and a much slower change in the water column due to the removal mechanisms and the water column-sediment interactions. The response time is therefore a function of how long the load into the lake has been occurring with consequent transport of the toxicant to the sediment. If there is no sediment interaction, then, of course, the water column response depends only on the net settling velocity and other losses. With sediment interaction and considering the load to have been discharged over a time sufficient to contaminate the sediment then the water column will continue to receive a flux from the sediment and response times will be lengthened.

The calculated response times for plutonium and the five Lakes under two conditions on the water column - sediment interaction are shown in Figure 41. These plots were calculated assuming that at the end of 1973 (i.e. at the end of the 20 year loading pattern), the external input of plutonium is eliminated; the results, therefore, represent the responses due to an instantaneous elimination in the external load. The concentrations shown at t=0 are those at the end of 1973. The response times include the effects of hydraulic residence, vertical settling of particulates and interaction with the sediments.

The most striking aspect of these calculations is the range in response times under different conditions on sediment resuspension. For example, for Lake Michigan, if no sediment resuspension is included (i.e. $w_a = w_{net}$), the 50% response time (i.e. the time to reach one half of the initial value) is less than 5 years and the plutonium clears out rapidly. With resuspension from a 2 cm sediment layer; however, a condition used in the preceding solids and plutonium balance, the 50% response time is extended by about an order of magnitude. In Central Lake Erie, with the sediment as a sink (no resuspension), the 50% response time is less than one year; whereas with suspension, the response time increases to greater than 5 years.

Note that these response times are markedly different than the times associated with the calculated plutonium history during the period of 1953-1965. Figure 24 shows a peak load in 1963 with a rapid decline by almost one order of magnitude within about 8 years. The water column response shown in Figure 25 paralleled this decline but levelled off as a result of the sediment resuspension included in the calculation. Also Figure 17 shows that for Lake Michigan the sediment particulate concentration reached an approximate equilibrium by about 1965.



41. Calculated time history for ^{239,240}Pu load reduced to zero after 1971 for two conditions on water column-sediment interaction: $w_a = w_n$ (resuspension = zero) and $w_a - 2.5$ m/d.

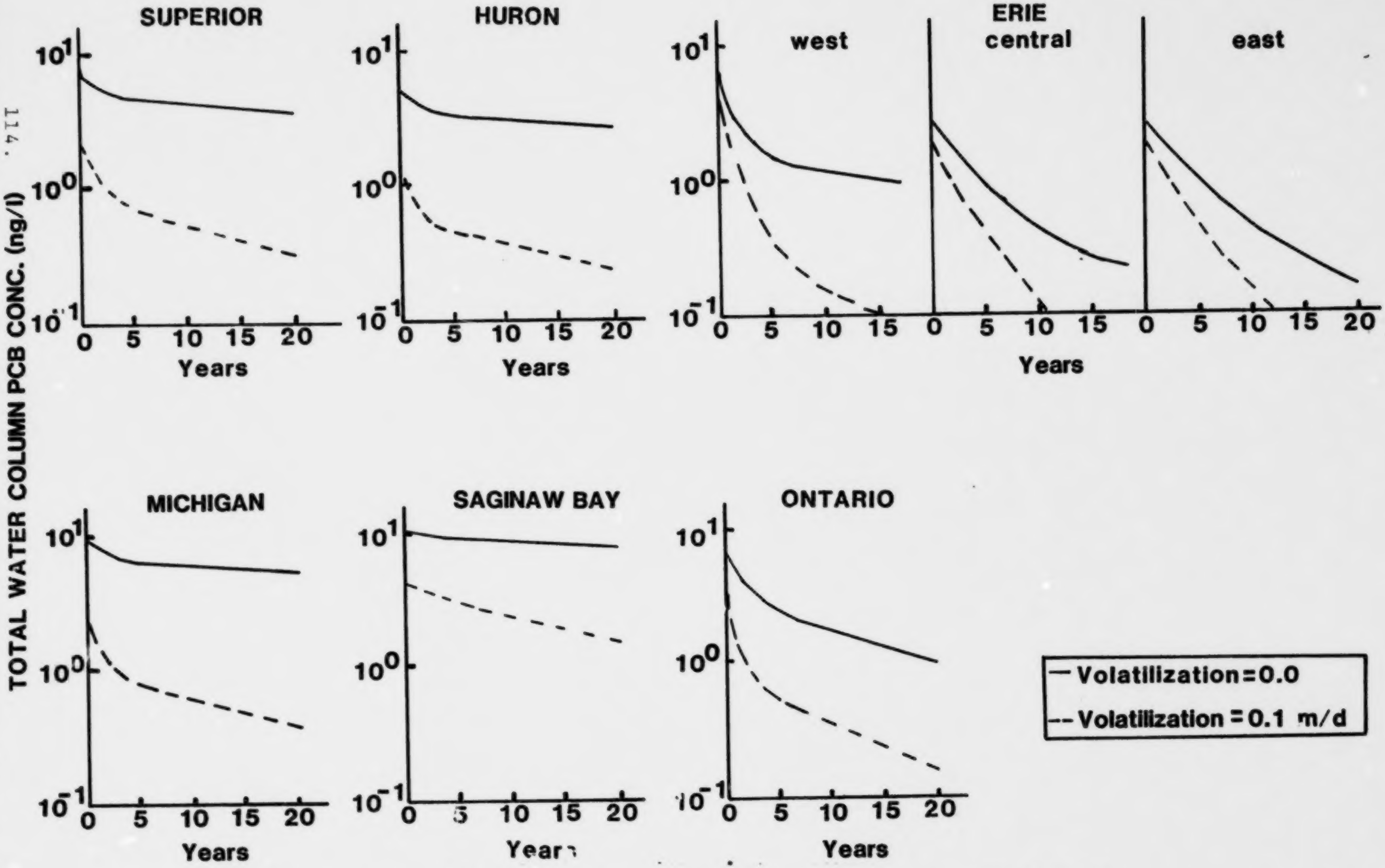
PCB

It is also informative to simulate the response of PCB levels in the Lakes due to a reduction in loading after the water column sediment have reached the levels shown in Figures 36 and 37. Such a simulation for the upper load level is shown in Figures 42 and 43. In this calculation, all solids and sediment interactions are as previously used for the plutonium model where resuspension is included. The external PCB load is assumed to drop to zero following the attainment of equilibrium. The two conditions used in the simulation include the case of no volatilization of PCB and a volatilization exchange rate of 0.1 m/d. As shown in Figures 42 and 43 for the water column and sediment respectively, the effect on the response time of volatilization is marked. For example, for Lake Michigan, the time to decline to 50% of the intial concentration varies from 15-20 years without volatilization to 1-2 years with volatilization. The relatively rapid response of Lake Erie under both conditions is also clearly indicated by Figures 42 and 43. It can also be noted that the sediment concentration decline parallels the water column concentration. A comparison of these response times can be made to the response of fish concentrations of PCB (IJC, 1981). For eastern Lake Michigan bloaters, the time for PCB concentrations to decline by one-half beginning in 1972 is about 5 years. This decline may be presumed to reflect a reduction in external load. Form this comparison, it is concluded that volatilization of PCB is occurring at an exchange rate of approximately 0.1 m/d for Lake Michigan.

Conclusions

It is concluded from these calculations of response times that for large lakes such as Michigan where response times are relatively long, a water column/sediment equilibrium model is not appropriate since the sediment response time is markedly different than the water column. The inclusion of sediment resuspension and interaction increases the response time of a nonreactive but particulate sorptive substance such as plutonium by about an order of magnitude over the case where resuspension is assumed to be zero.

For PCB, the response times due to load reduction of external sources of PCB may vary by an order of magnitude depending on the magnitude of the volatilization exchange rate; 50% response times vary from a few years with volatilization to 5-10 years or longer without volatilization. Comparison of these response times to observed declines in concentrations of PCB bloaters indicate that volatilization of PCB is occurring at an exchange rate of about 0.1 m/d at least for that lake.



42. Calculated water column PCB concentration response to an instantaneous drop in upper level PCB load at time t = 0.

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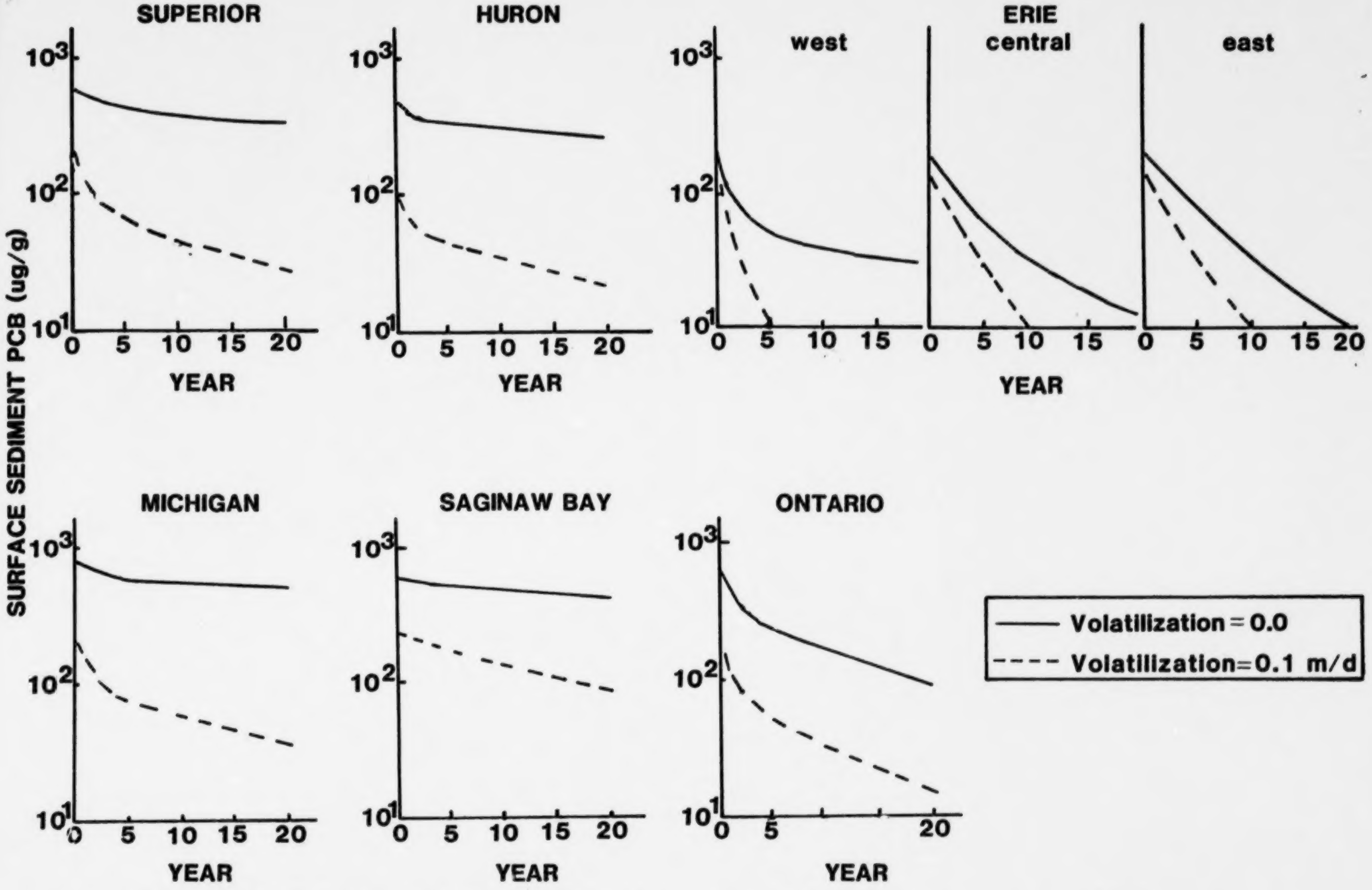
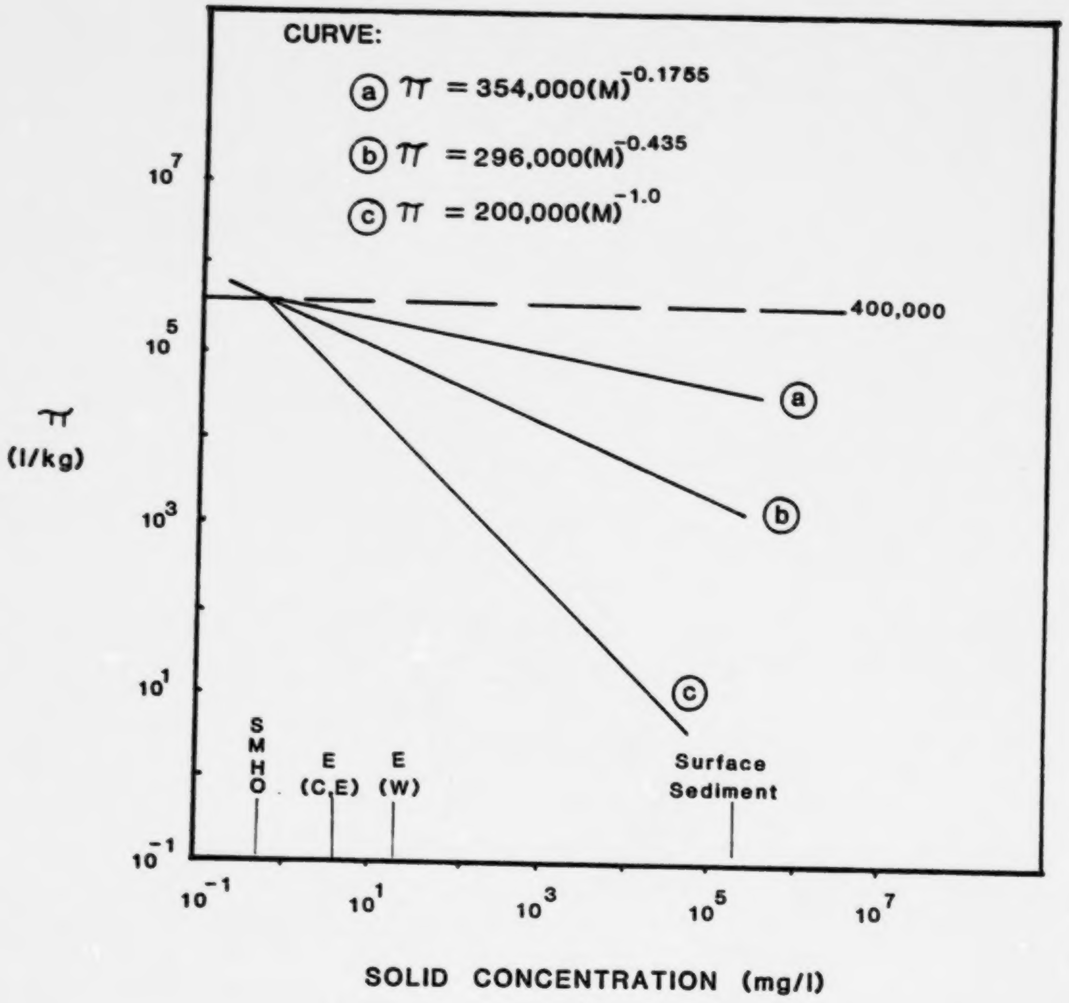


43. Calculated surface sediment PCB concentration response to an instantaneous drop in upper level PCB load at time t = 0.



44. Assumed variation of plutonium partition coefficient with solids concentration used in sensitivity analysis.

SECTION 10
EFFECT OF SOLIDS DEPENDENT PARTITIONING AND SEDIMENT DIFFUSION

INTRODUCTION

It has been noted by O'Connor and Connolly (1980) in a summary of the literature that there is for some chemicals an apparent dependence of the partition coefficient on the concentration of solids. The mechanisms for this dependence are not clear but may be related to some interaction between solids which affects the available sites for sorption. The dependence of the partition coefficient on solids concentration had also been noted by Seymour, et al (1979) for Americium-241.

O'Connor and Connolly (1980) analyzed a variety of data relating partition coefficient to solids concentration using the general form of

$$\pi = \pi_\infty + \frac{b}{m_o + m^\alpha} \tag{80}$$

where π_∞ is the lower limiting partition coefficient at high solids and m_o bounds the upper limiting partition coefficient at low solids concentration. Assuming that π_∞ and m_o are zero and generally over the range of solids from $10\text{-}10^4$ mg/ℓ O'Connor and Connolly (1980) computed values for α ranging from 0.19 to 0.92. The work of Seymour, et al. (1979) resulted in α values of 1.4 for desorption of Americium and 2.0 for adsorption.

If a chemical displays an inverse dependence of partition coefficient on the concentrations of solids, then at the high solids concentrations found in bed sediment, the partition coefficient would be expected to be lower than for the water column. Less chemical would then be sorbed onto sediment particles and an increase in interstitial dissolved chemical would occur. A gradient between the dissolved chemical in the bed and the dissolved chemical in the overlying water would then develop and depending on the magnitude of the exchange between the sediment and water column, a flux of the chemical from the sediment to the water may occur. In this section, the sensitivity of the previous plutonium and PCB calculations to this effect is calculated and discussed.

SENSITIVITY OF PLUTONIUM CALCULATION

No laboratory data were available on the dependence of the plutonium partition coefficient on solids concentration. Accordingly, three relationships were examined where, in all cases, the partition coefficients was fixed at 400,000 ℓ/kg at a solids concentration of 0.5 mg/ℓ and the slope of the change in partition coefficient with solids concentration was varied. The three relationships as showin in Figure 44 are

(a) $\pi = 354{,}000\ (M)^{-.1755}$; a one order of magnitude decrease from 0.5 mg/ℓ to surface sediment concentrations of 240,000 mg/ℓ

(b) $\pi = 296{,}000\ (M)^{-.435}$; a slope equal to that used for the PCB sensitivity analysis (discussed subsequently)

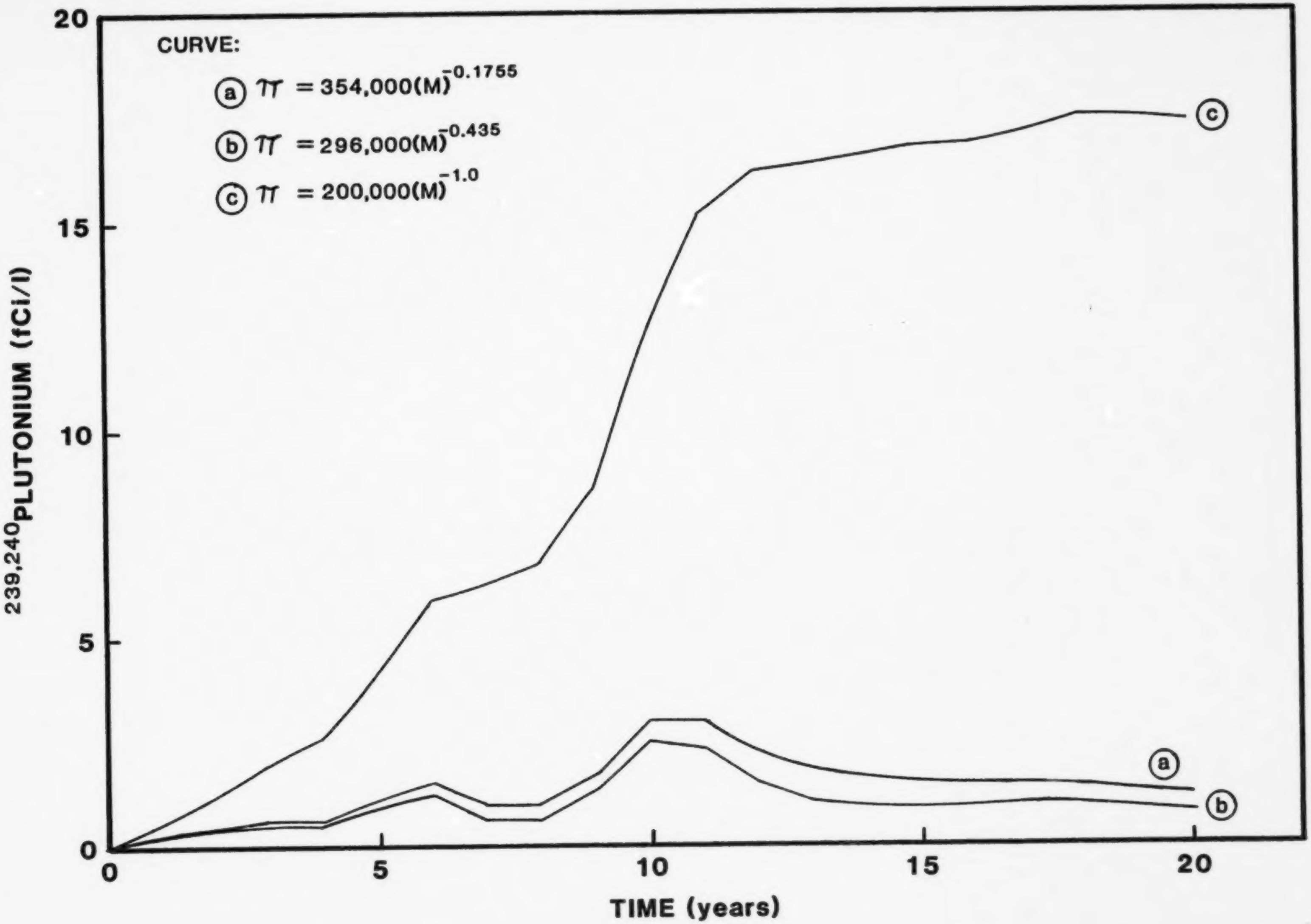
(c) $\pi = 200{,}000\ (M)^{-1.0}$; an approximate upper bound of the slope.

A sediment diffusion coefficient of 10^{-5} cm^2/sec (Hesslein, 1980; Lerman and Weiler, 1970; Lerman and Lietzke, 1975) was used throughout all calculations.

Figure 45 shows the sensitivity of the 20 year plutonium calculation for Lake Michigan to the three assumed relationships. The data as shown in Figure 26 indicate that the ^{239,240}Pu concentration in the years 1971 -1973 (years 18-20) is less than 1 fci/ℓ. The sensitivity of the mass dependent effect with a slope of -1, (curve c in Figure 44) is most marked and results in a completely different time dependence and equilibrium values that are substantially greater by more than one order of magnitude then the observed data. This is due to the increased dissolved plutonium, (by about an order of magnitude) and subsequent flux to the overlying water column. It is also interesting to note that the increase in water column concentration is not directly related to the slope of the mass dependent relationships since curve "b" results in a lower concentration in the water column than curve "a." Based on Figure 45 and the observed data in Figure 26, it is concluded from the sensitivity analysis that a dependence of partition coefficient on solids concentration at a slope of -1 is too high and results in calculated water column concentrations that are about an order of magnitude higher than observed data. Further sensitivity runs were therefore made using curve "b" (slope of -.435) as approximately representative of the solids dependent effect.

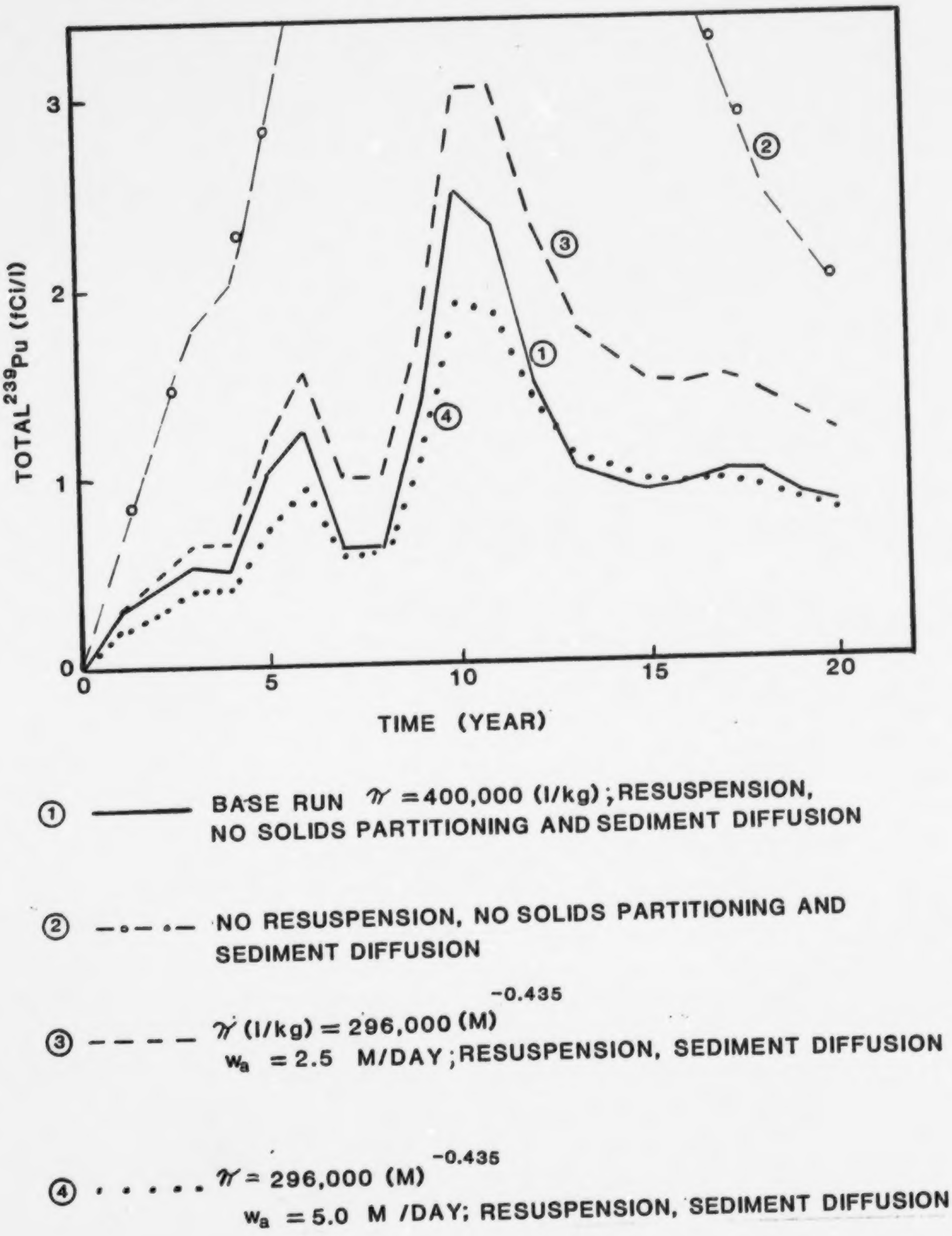
Figure 46 summarizes earlier calculations and the sensitivity of the solids dependence for Lake Michigan. The base run with resuspension consistent with a settling velocity of 2.5 m/day has already been compared to the case of no resuspension and no diffusion (curve 2). As shown, including solids dependent partitioning (curve 3) results in a higher concentration over the base run case due to sediment diffusion. The question addressed at this point then was "Could an equally good calibration to observed data be obtained with sediment diffusion but increased settling velocity of particulate from the water column?" Curve 4 indicates that indeed increasing the particulate settling velocity to 5 m/day and maintaining solids dependent partitioning can give an approximately equivalent calibration. In the total concentration of plutonium in the water column then it is not possible to distinguish the appropriate settling velocity from the appropriate sediment diffusion and, therefore, one must look to other representations of the plutonium to determine any change as a result of the trade-off between particulate settling velocity and solids dependent partitioning.

Figure 47 shows the particulate concentration in the water column and sediment under three conditions, a) partitioning independent of solids concentration, b) solids dependent partitioning and $w_a = 2.5$ m/day, c) solids dependent partitioning and $w_a = 5$ m/day. Including

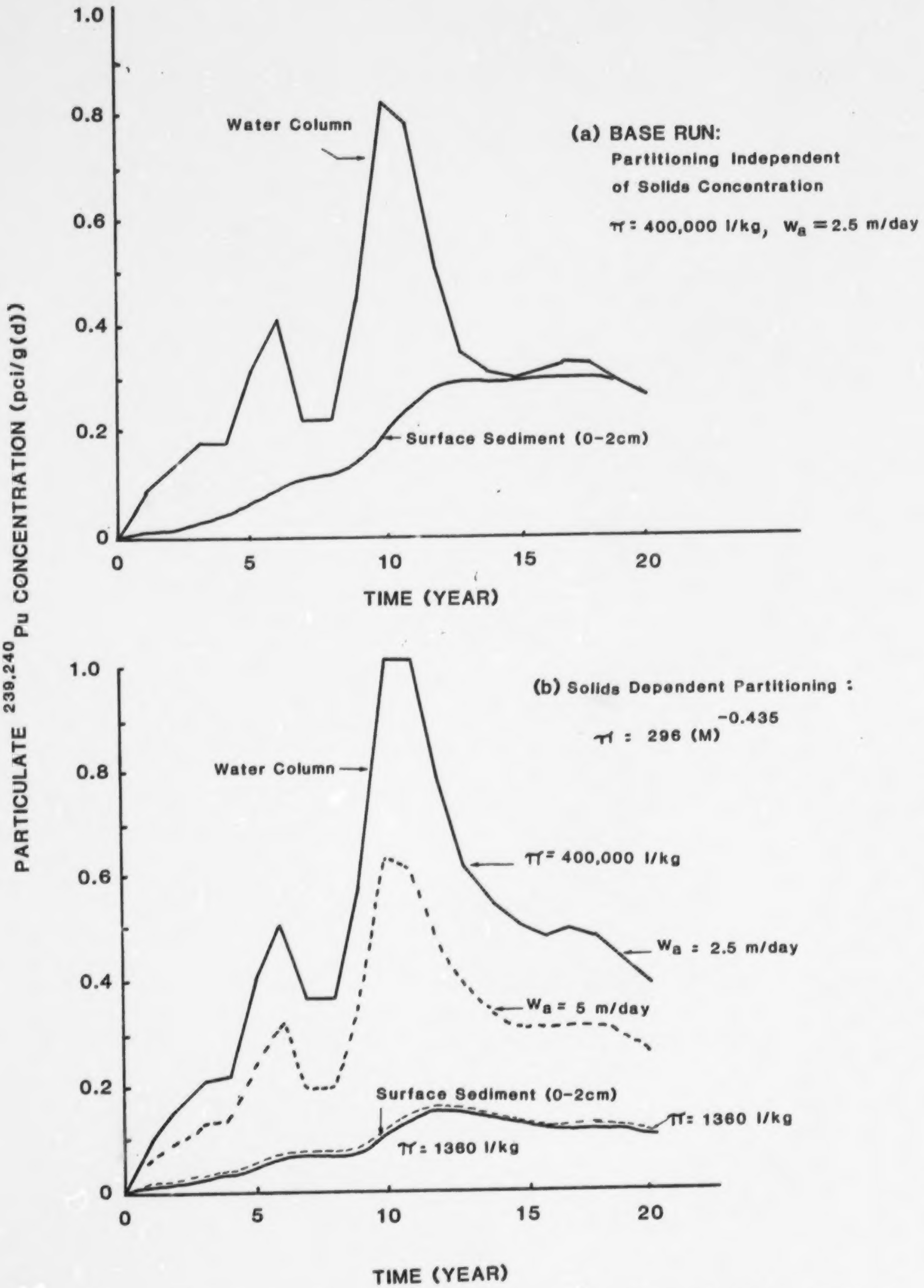


45. Sensitivity of total plutonium water column concentration for Lake Michigan to three assumptions on mass dependence of partition coefficient (see Figure A).

(45)



46. Comparison of Lake Michigan plutonium total water column concentration calculations under different assumptions on particulate settling.



47. Calculated variation of Lake Michigan particulate plutonium concentration in water column and surface sediment: (a) base run, (b) with solids dependent partitioning and w_a = 2.5 and 5.0 m/d.

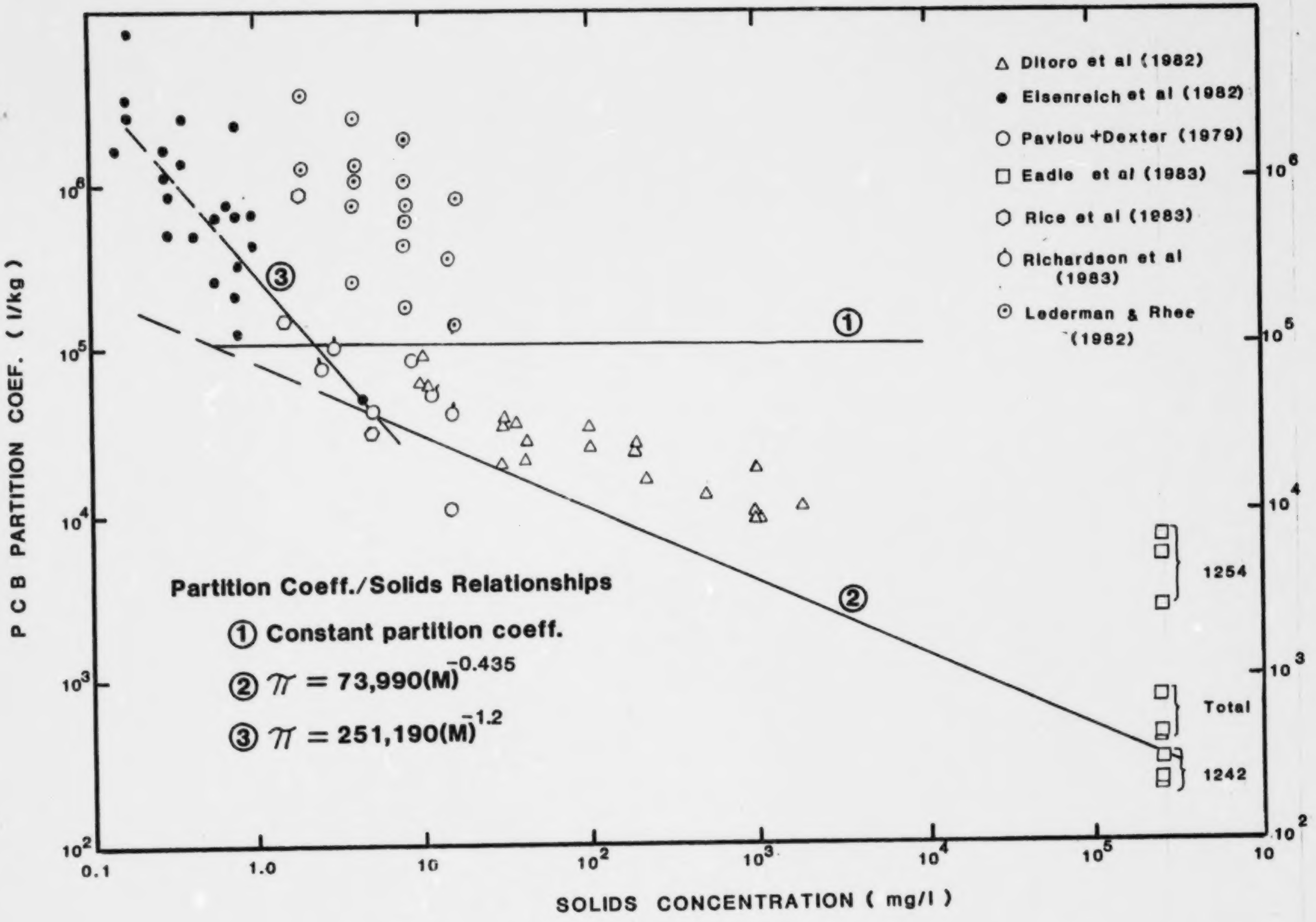
solids dependent partitioning in the base run case increased the particulate plutonium concentration in the water column even though the partition coefficient at water column solids concentration (0.5 mg/ℓ) was the same as for the base run (400,000 ℓkg). This is due to the fact that the increased flux of dissolved plutonium from the sediment increases the sorption onto the particulates. Surface sediment concentrations, however, decrease by almost one-third and bracket the surface sediment data shown in Figure 27. Note that in Figure 47(b), the water column particulate concentration is about 3-4 times sediment concentration reflecting the disequilibrium between water column and sediment under time variable conditions. Although one might have hoped that the particulate plutonium concentration would be definitive in separating out particulate settling and diffusion effects such is not the case. Figure 47(b) does indicate, however, that if detailed data were available on the water column particulate concentration and surface sediment concentration that a determination could be made in principle of the appropriate settling velocity and solids dependence.

It is, therefore, concluded form this sensitivity analysis that particulate settling velocities of 2.5-5.0 m/day, with or without solids dependent partitioning (at a log slope of -.435) and sediment diffusion provide an approximately equal representation of the observed plutonium data. As noted earlier, a more marked solids dependence (log slope of -1) of the partition coefficient does not provide an acceptable comparison to the observed data.

SENSITIVITY OF PCB CALCULATION

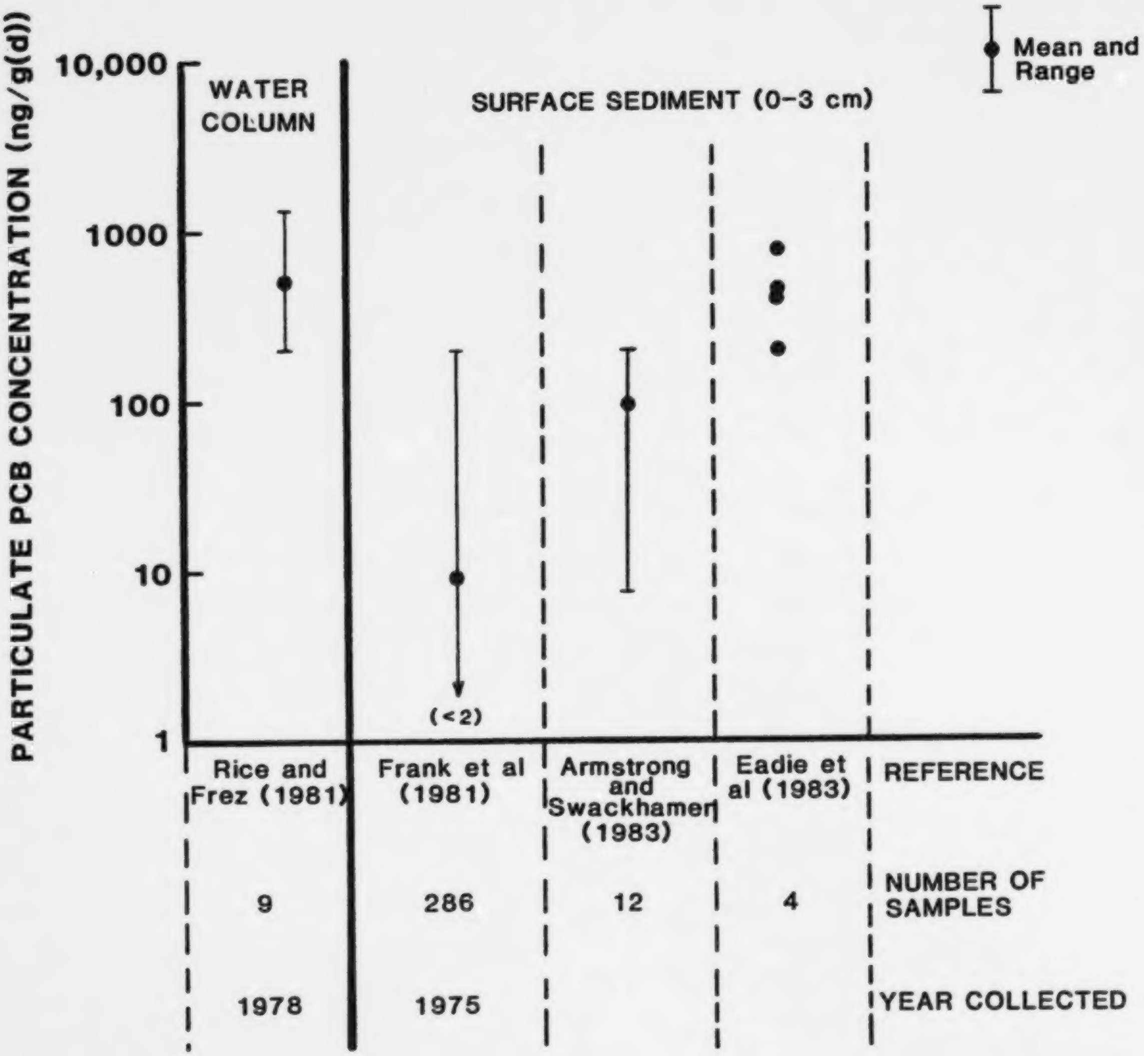
Figure 48 shows a compilation of PCB partition coefficients as a function of solids concentration ranging from approximately 0.1 mg/ℓ as reported for Lake Superior (Eisenreich, et al., 1983) to Lake Michigan sediment solids of 200,000 mg/ℓ as reported by Eadie, et al. (1983). The data indicate a dependence of the PCB partition coefficient on solids concentration where for concentrations at about 10 mg/ℓ and higher, the partition coefficient declines logarithmically at a slope of about -0.435. This depends heavily, however, on the one point of a sediment partition coefficient reported by Eadie, et al. (1983). The data of Di Toro, et al. (1982) indicate, for Saginaw Bay sediments, that the partition coefficient may be leveling off at about 10^4 ℓ/kg at solids concentrations greater than about 1000 mg/ℓ. The data of Eisenreich, et al. (1983) for Lake Superior extend into the concentration of solids at less than 1 mg/ℓ and show a steep increase in partition coefficient at the lower solids concentration. The data from Lederman and Rhee (1982) are for Great Lakes algae and the higher partitioning may reflect the presence of lipids in the algae.

If the partition coefficients differ between the water column and the sediment, then one would expect the particulate PCB concentration in the water column to be higher than that of the sediment. There is some evidence to indicate that this may be the case for Lake Michigan as shown in Figure 49. Rice and Frez (1981) reported water column particulate PCB concentrations ranging from 213 ng/g(d) to 1147 ng/g(d) with indications



48. Summary of reported PCB partition coefficients and solids concentrations and relationships assumed in sensitivity analyses.

49



49. Comparison of measured particulate PCB concentration in water column and surface sediment, Lake Michigan.

of a decrease of the concentration with depth. The average of their data is 537 ng/g(d). The surface sediment PCB data as shown in Figure 49 varies by an order of magnitude although it should be recognized that the data of Frank, et al. (1981) represents 286 samples throughout the Lake while Armstrong and Swackhamer (1983) and Eadie, et al. (1983) represent only 12 and 4 samples respectively. If the data of Frank, et al. (1981) is used then there is about a two order of magnitude decrease in the particulate PCB concentration between the water column and the sediment. In the model used here, the only way that such a decrease can be calculated is through a solids dependent partition coefficient.

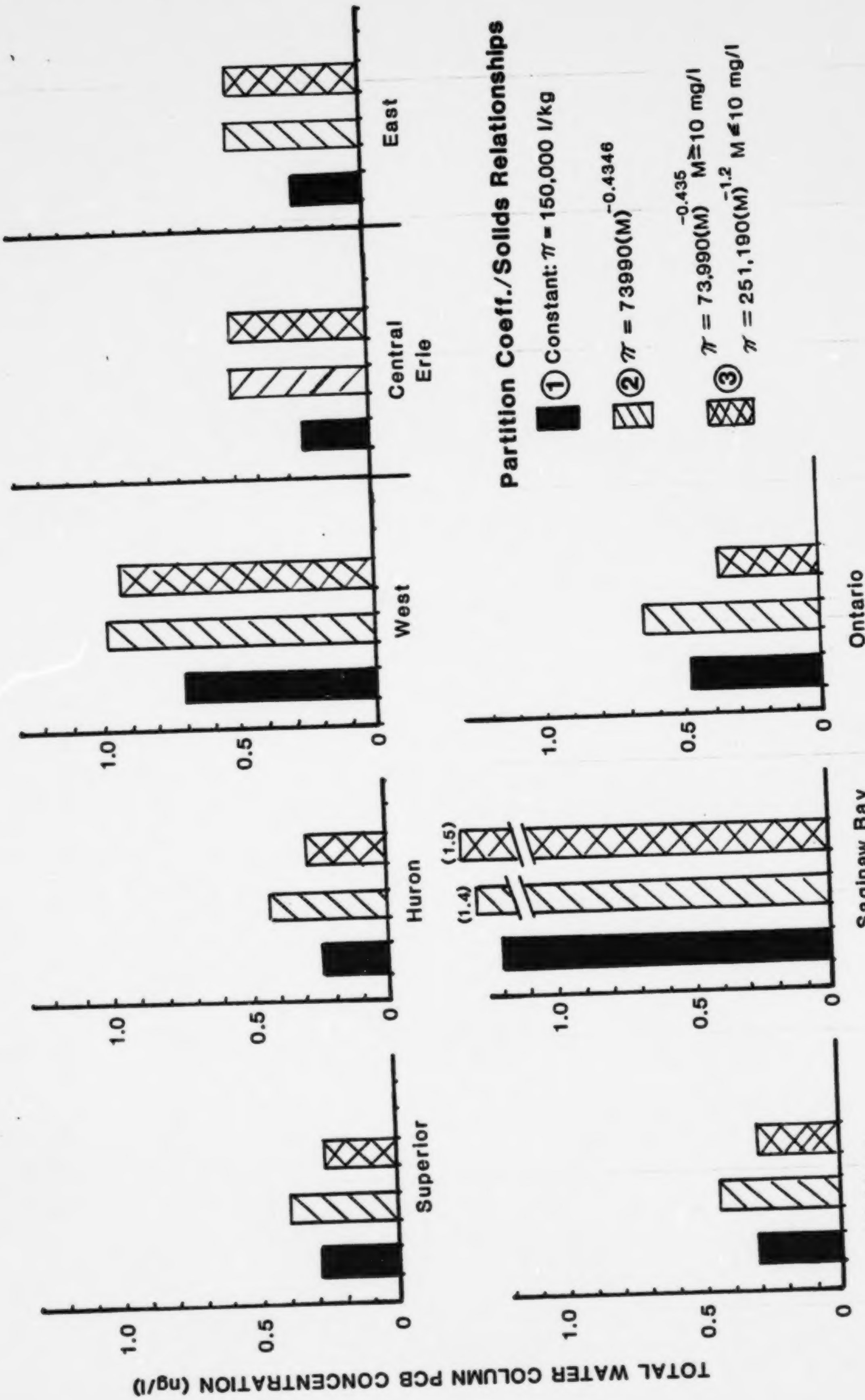
Two cases ot solids dependent partitioning of PCBs were therefore examined:

a) $\pi = 73{,}990\ M^{-.435}$
and b) $\pi = 25{,}120\ M^{-1.2}$ for solids < 10 ng/ℓ
$\pi = 73{,}990\ M^{-.435}$ for solids ≥ 10 ng/ℓ

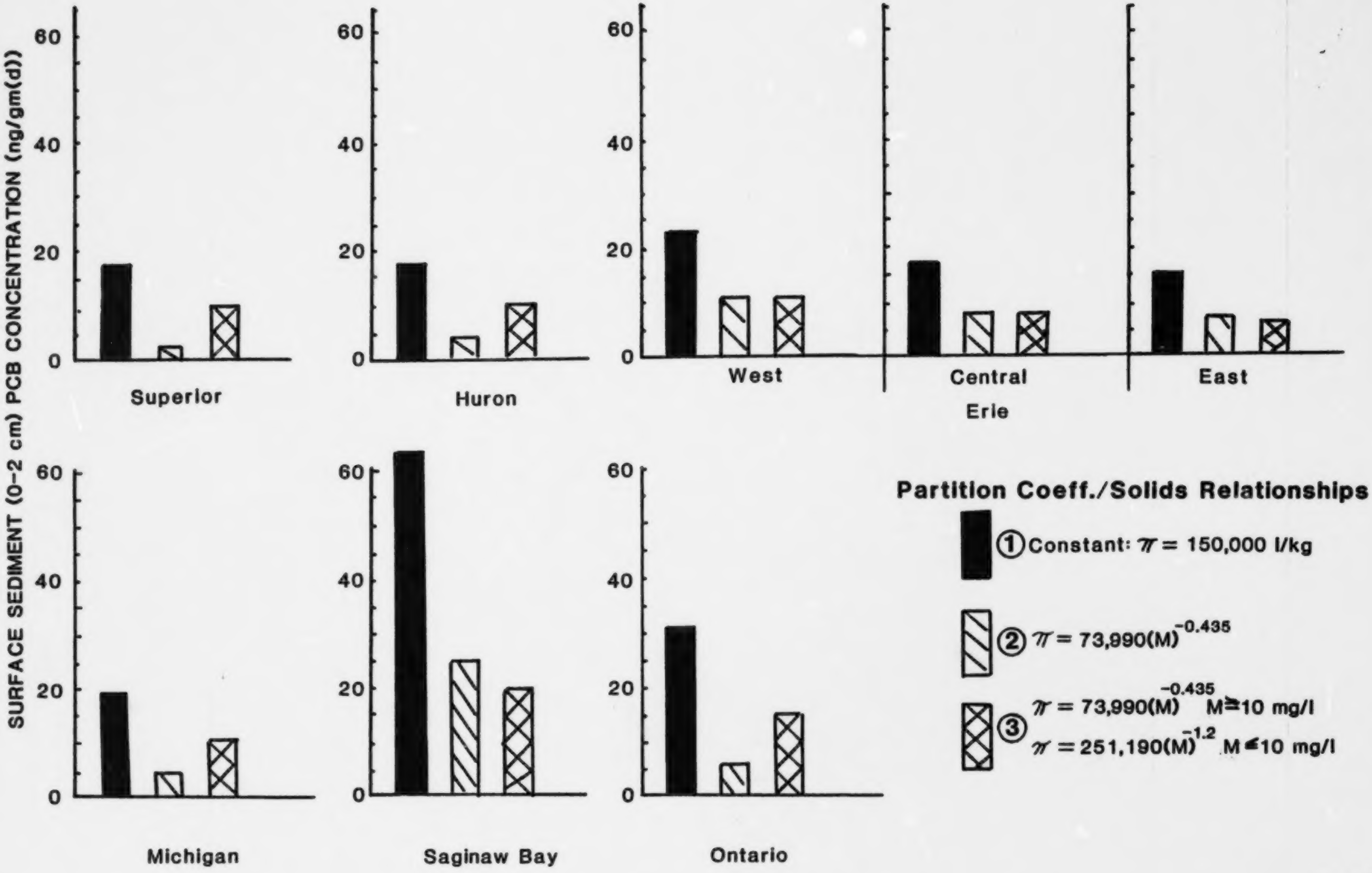
Figures 50 through 53 summarize the results under the lower level of loading of PCBs and including volatilization. Several points can be noted. As shown in Figures 50 and 51, the total and dissolved water concentrations are not sensitive in a significant way to the assumption on partitioning. The principal effect on the dissolved component is in Western Lake Erie where the dissolved concentration increases by a factor of three. In all other lakes, however, for practical purposes, the total and dissolved concentrations are unaffected by the partitioning assumption. Figure 52 shows that the surface sediment concentration is also not markedly affected (to order of magnitude) by the partitioning assumption although a decline of about 50% is evident in the lake sediment and a decline of about 70% is calculated for the surface sediment of Saginaw Bay.

These reductions in sediment PCB particulate concentration reflect the assumed reduced partitioning at the high solids concentrations and are, therefore, subsequently reflected in the PCB concentration of the interstitial water of the surface sediment as shown in Figure 53. It is in the interstitial water that the effect of the solids dependent partitioning is most pronounced. Here increases in the dissolved PCB concentration of about two orders of magnitude are calculated as seen in Figure 53.

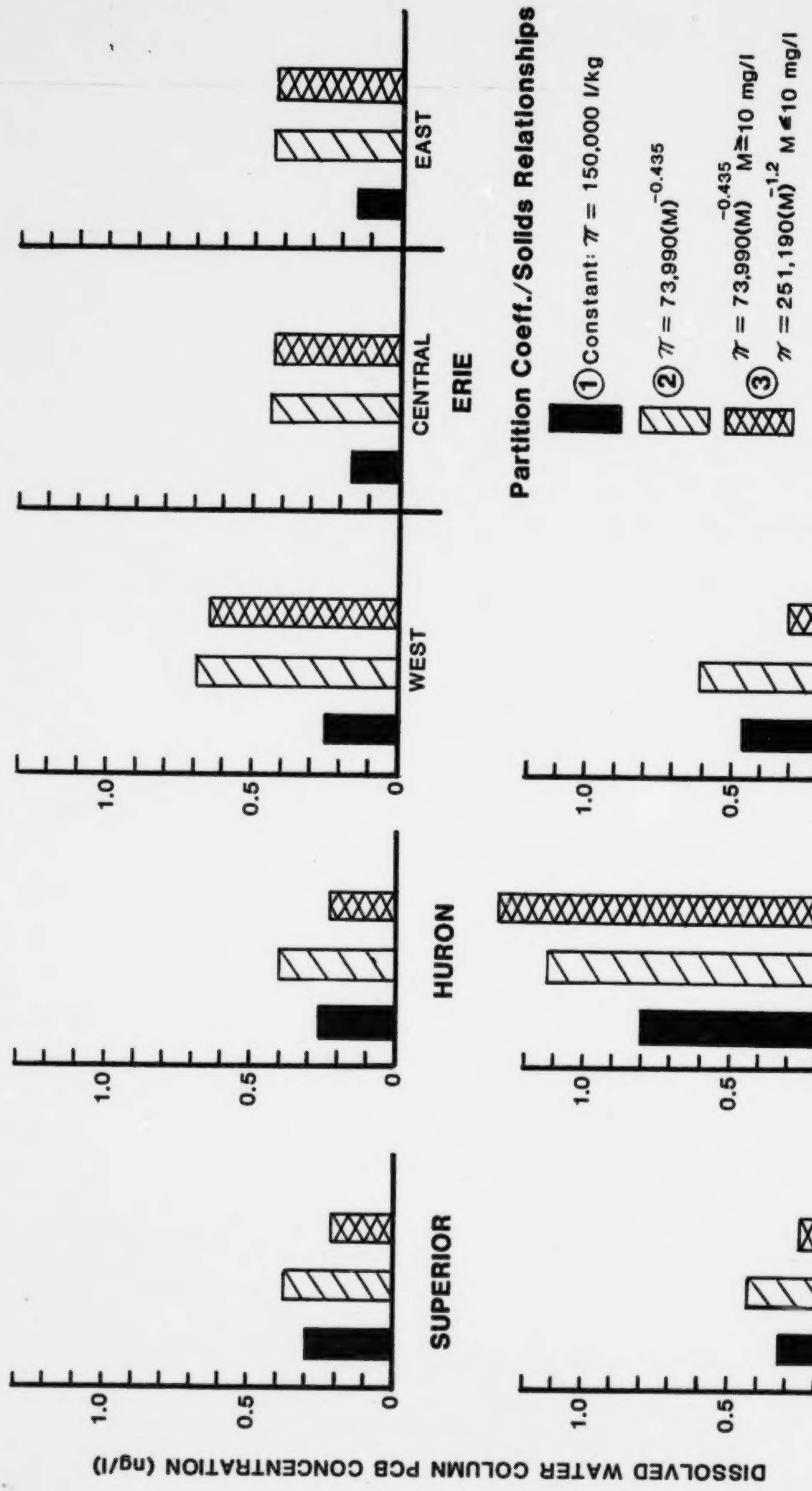
For Lake Michigan, as an example, the interstitial concentration of PCB as calculated for a constant partition coefficient is about 0.25 ng/ℓ. For a variable partition coefficient (Relationship No. 3 in Figure 53), the concentration increases to about 30 ng/ℓ. Eadie, et al. (1983) reported values of pore water PCB at three stations in southern Lake Michigan of 159, 214, and 342 ng/ℓ which is about one order of magnitude higher than that calculated in Figure 53. However, the estimate shown in that Figure 53 represents a lake-wide average incuding regions of non-deposition. One would, therefore, expect an observed lake-wide average to be less than individual core samples. Indeed, the high value of 342 ng/ℓ reported by Eadie, et al. (1983) is for a station off Benton Harbor, Michigan with the highest recorded accumulation rate in Lake Michigan of 3 g/m^2/day. This accumulation is 16 times the lake-wide average net dep-

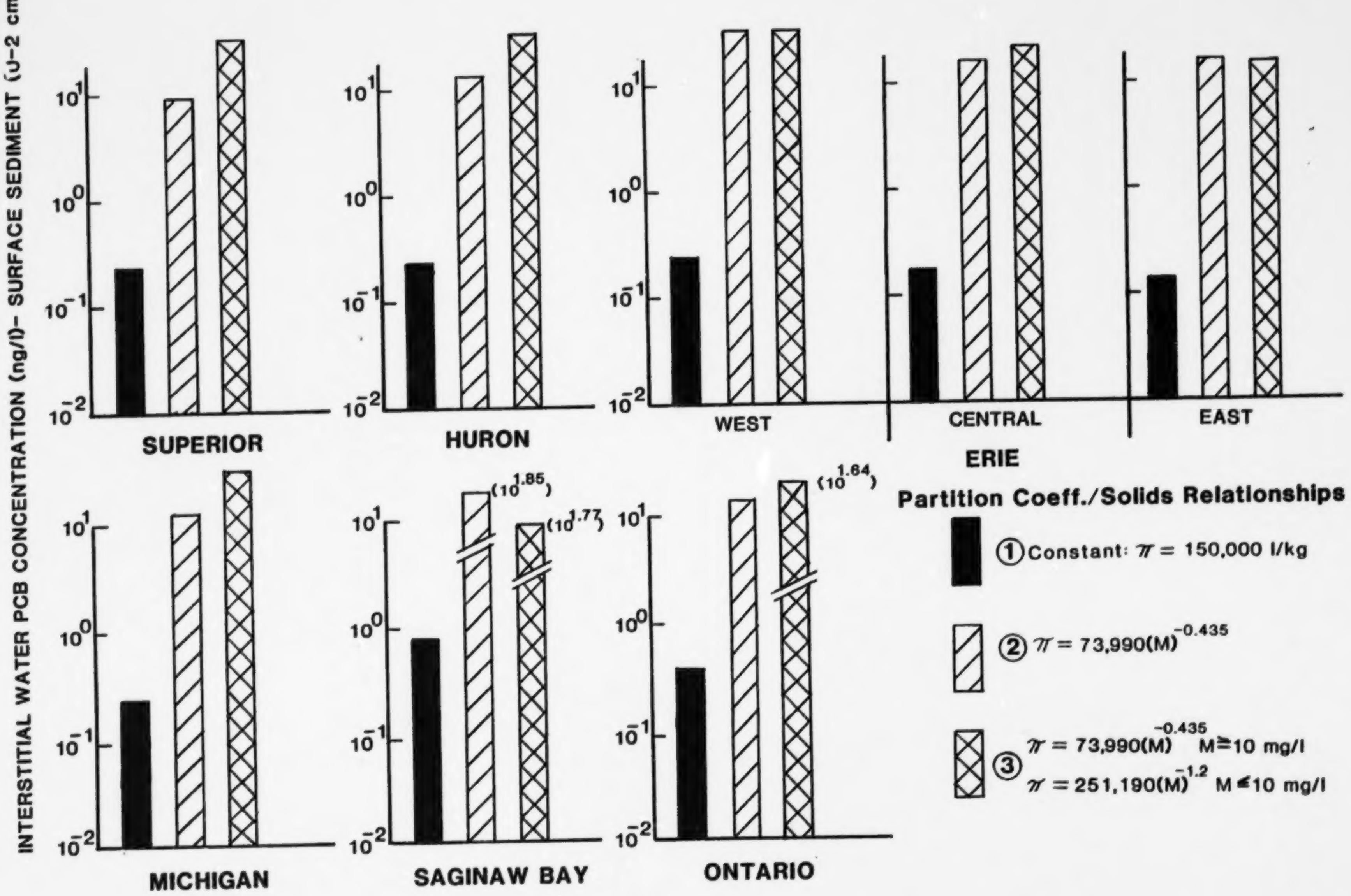

TOTAL WATER COLUMN PCB CONCENTRATION (ng/l)
1.0
0.5
0
Superior
Huron
West
Central Erie
East
Michigan
Saginaw Bay
Ontario
(1.4)
(1.5)
Partition Coeff./Solids Relationships
① Constant: π = 150,000 l/kg
② π = 73990(M)^-0.4346
③ π = 73,990(M)^-0.435 M≥10 mg/l
π = 251,190(M)^-1.2 M≤10 mg/l

⑤


SURFACE SEDIMENT (0–2 cm) PCB CONCENTRATION (ng/gm(d))
60
40
20
0
Superior
Huron
West
Central
East
Erie
Michigan
Saginaw Bay
Ontario
Partition Coeff./Solids Relationships
① Constant: π = 150,000 l/kg
② π = 73,990(M)^-0.435
③ π = 73,990(M)^-0.435 M≥10 mg/l
π = 251,190(M)^-1.2 M≤10 mg/l

2


DISSOLVED WATER COLUMN PCB CONCENTRATION (ng/l)
1.0
0.5
0
SUPERIOR
HURON
WEST
CENTRAL
EAST
ERIE
MICHIGAN
SAGINAW BAY
ONTARIO
Partition Coeff./Solids Relationships
① Constant: π = 150,000 l/kg
② π = 73,990(M)^-0.435
③ π = 73,990(M)^-0.435 M≥10 mg/l
π = 251,190(M)^-1.2 M≤10 mg/l


INTERSTITIAL WATER PCB CONCENTRATION (ng/l)- SURFACE SEDIMENT (0-2 cm)
10^{1}
10^{0}
10^{-1}
10^{-2}
SUPERIOR
HURON
WEST
CENTRAL
EAST
ERIE
MICHIGAN
SAGINAW BAY
ONTARIO
$(10^{1.85})$
$(10^{1.77})$
$(10^{1.64})$
Partition Coeff./Solids Relationships
① Constant: $\pi = 150,000$ l/kg
② $\pi = 73,990(M)^{-0.435}$
③ $\pi = 73,990(M)^{-0.435}$ $M \geq 10$ mg/l
$\pi = 251,190(M)^{-1.2}$ $M \leq 10$ mg/l

osition as used in the preceding solids balance calculation. It can also be noted that the calculation shown in Figure 53 is for the low loading condition for PCB. The higher loading condition would result in an increase in interstitial water PCB concentration approximately proportional to the load or a factor of about 7 over the lower load condition.

In any event, it appears from this calculation on the sensitivity of the PCB distribution in the Great Lakes to a sediment dependent partition coefficient that:

(1) such a relationship is more representative of the observed particulate and sediment PCB data in Lake Michigan;

(2) total and dissolved PCB concentration in the water column and sediment PCB concentration are not affected significantly (i.e. by at least one order of magnitude) under a solids dependent partitioning assumption;

(3) interstitial PCB concentration in the sediment is affected markedly by such an assumption and an increase of about two orders of magnitude is calculated.

(4) since the increased interstitial PCB concentration in the sediment is about two orders of magnitude higher than the overlying water dissolved PCB concentrations, one would expect benthic organisms to carry a significantly higher body burden than organisms exposed solely to the water column and as a result would be a potential significant source of PCBs to top predators in the food chain.

Since the interstitial PCB component is potentially significant and since the issue of solids-dependent partitioning is of contemporary interest on constructing mass balances of PCB, it is recommended that additional sampling of pore water PCB and PCB concentration in benthic organisms be conducted in various Great Lakes regions.

SECTION 11

APPLICATION OF MODEL TO BENZO (a) PYRENE AND CADMIUM

As noted in the earlier Sections of this report, the physico-chemical model is developed to provide a means for assessing the fate of chemicals entering the Great Lakes system. The credibility of such a model depends to some considerable degree on the ability of the framework to explain observed chemical concentrations. The preceding Sections dealt with the use of plutonium as a calibrating variable for the model and also the application to PCBs, a contemporary chemical of some interest. In this Section, the model is further applied to two other chemicals: a) benzo(a)pyrene, a polycyclic aromatic hydrocarbon (PAH), and b) cadmium, a representative metal. For both chemicals some data exist for the application of the model framework.

BENZO(a)PYRENE

The distribution of this chemical, one of the PAH compounds resulting from incomplete combustion of organic materials has been widely studied (Neff, 1979) because of its potential carcinogenicity. The fate of benzo(a)pyrene (BaP) in the Great Lakes has recently been evaluated in a series of papers by B.J. Eadie (Eadie, et al., 1982; Eadie, 1983; Eadie, et al., 1983). In that work, data are presented for the range of concentration of BaP in the water column and surficial sediments as well as preliminary data on the BaP concentration in the pore water of the sediment. It is those data (together with estimates of loading) that can be used as a further application of the physico-chemical model.

Table 20 shows some of the basic chemical properties of BaP.

TABLE 20
CHEMICAL PROPERTIES OF BENZO(a)PYRENE
(From Neff, 1979)

Molecular Weight - 252

Vapor Pressure (mmHg) - $5.49 \cdot 10^{-9}$

Saturation Vapor Concentration ($\mu g/1000\ m^3$) - 75

Water Solubility ($\mu g/\ell$) - 0.172(1977)[1]; 0.5 (1971); 6.05(1946; 4.0 (1942)

[1] Date parentheses is date of publication as cited in Neff (1979)

As seen, BaP is sparingly soluble in water (especially if the more contemporary value of solubility is accepted) and as such would be expected to have an affinity for solids. The partitioning on to particulates and in addition, the extent of volatilization of the BaP must be estimated. Although BaP is known to undergo photolysis (Neff, 1979) this pathway is not considered in this application.

BaP Loads

As discussed in Eadie (1983), the principal source of BaP is from the atmosphere. Eisenreich, et al. (1980) have estimated the airborne load to the Great Lakes and their estimates are shown in Table 21, together with the calculated areal loading rate.

TABLE 21
ATMOSPHERIC LOAD OF BaP TO GREAT LAKES
(From Eisenreich, et al. (1980))

Lake	Load 10^3 kg/yr	Area (km^2)	Areal Loading Rate g/km^2-yr
Superior	7.9	82882	95.3
Michigan	5.6	57772	96.9
Huron	5.8	61659	94.1
Erie	2.5	24996	100.0
Ontario	1.8	19485	92.4

As seen, the estimated atmospheric loading on an areal basis is about 95 g BaP/km^2-yr across all of the lakes but as noted by Eadie (1983), all BaP load estimates are based on quite limited data and therefore may vary as additional information becomes available.

Solids Partition Coefficient

Smith, et al. (1978) reported solids partition coefficients for BaP ranging from 17,000 to 150,000 ℓ/kg with a correlation to organic carbon (range .06 to 3.8%). Eqs. (31) and (34) with a solubility of 0.17 μg/ℓ and an organic carbon range of 5-10% yield coefficients from 9000 to 18,000 ℓ/kg which are lower by about an order of magnitude and therefore somewhat suspect.

From the data given in Eadie (1983) for Lake Michigan, a field value of π for BaP can be calculated to be between 143,000 and 287,000 ℓ/kg. The low estimate of 10,000 ℓ/kg is therefore probably not representative. However, like the PCB, the partition coefficient may be dependent on the solids concentration. From the limited data of Eadie (1983) the sediment partition coefficient can be estimated at about 600 ℓ/kg. The low solids concentration of Lake Michigan (<1 mg/ℓ) results in a considerably higher partition coefficient. In the absence of enough data to formulate a solids dependent partition coefficient, the model for BaP was run for π = 10,000 to 100,000 ℓ/kg, thereby providing a range of one order of magnitude in the solids partition coefficient.

Volatilization

For the conditions given in Table 19, the Henry's constant for BaP is calculated from

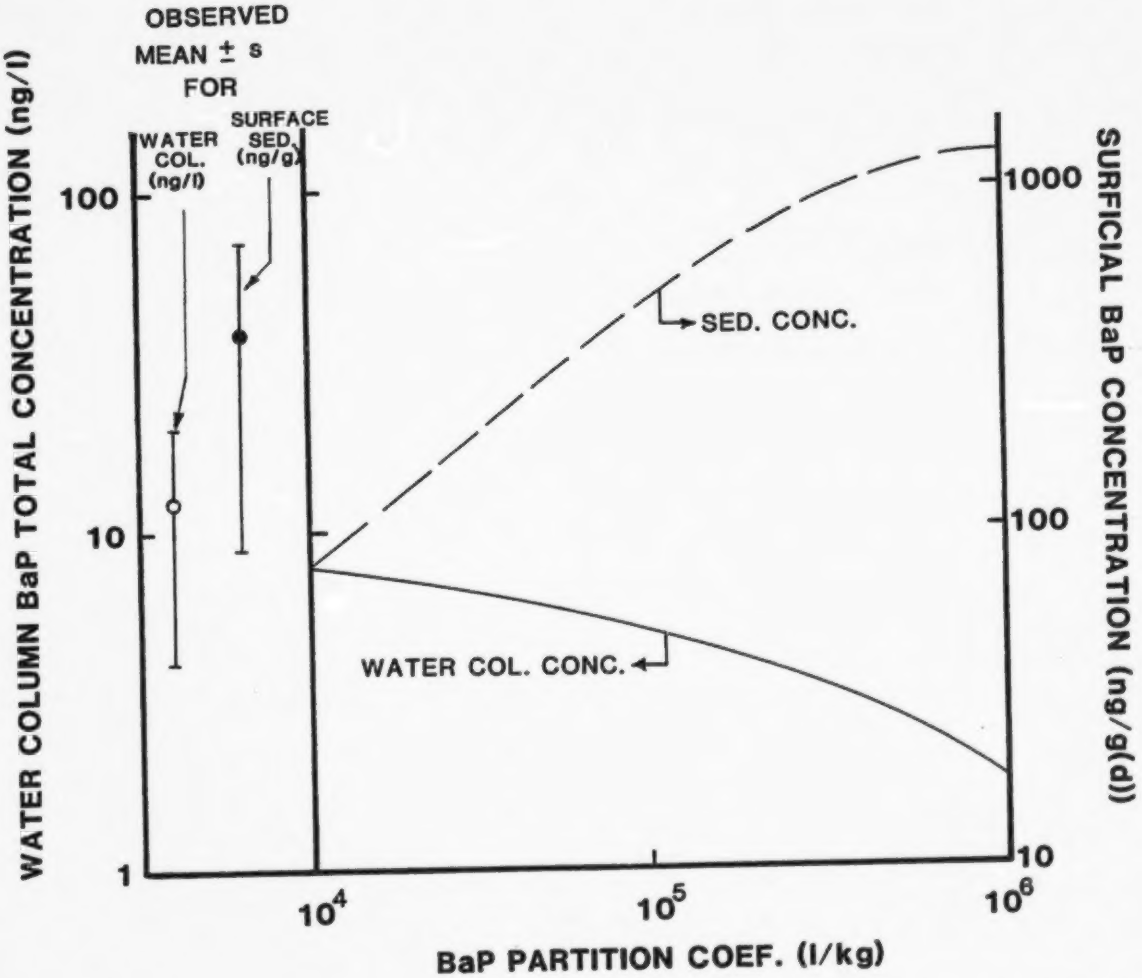
$$H_e = 16 \frac{M}{T} \frac{p}{c_w} \tag{81}$$

where M is the molecular weight, p is the partial pressure (mm Hg), c_w is the water solubility (mg/ℓ), T is temperature (°K) and H_e is the dimensionless Henry's constant and is calculated at $4.60 \cdot 10^{-4}$. Following Eqs. (7) and (8) and using a 4 m/s wind speed and diffusivity relationships to molecular weight as given in O'Connor (1982), the liquid film coefficient is calculated at 0.15 m/d and the product of the gas film coefficient and the Henry's constant is calculated at 0.040 m/d so that both the liquid and gas film control the volatilization of BaP. The overall water-air transfer coefficient is then calculated from Eq. (6) as 0.032 m/d and this value was used in the calculation.

Preliminary Calculations

The simplified steady state model discussed in Section 5 can provide a rapid means for calculating the in-lake and surface sediment concentration for BaP for an upstream lake such as Lake Michigan. (The concentration in the downstream lake can, of course, also be calculated given the upstream concentration; the concentrations in the overall Lake system are, therefore, best computed with the overall framework.) For Lake Michigan, water column BaP concentrations, Eq. (61) can be used with the estimate of the net loss of BaP given by Eq. (63) and the particulate BaP concentration can be calculated using Eq. (62). The net loss of the solids from Lake Michigan is taken from Table 10 at 137 m/yr. Since there is some uncertainty in the BaP partition coefficient as noted above, the steady state BaP concentration can be readily calculated over a range of coefficients and compared to observed data. The results of this steady state calculation are shown in Figure 54 where it is seen that at π for BaP of 10^4 (ℓ/kg), the calculated water column concentration is within the observed data but the surficial sediment concentration is low by

(57)



54. Steady state water column and surface sediment BaP concentrations compared to observed data from Eadie (1983).

almost an order of magnitude. At $\pi = 10^5$ ℓ/kg, the calculated surficial sediment concentration is approximately equal to the observed data, but the water column concentration is lower than the observed mean by a factor of about two but is still within the mean ± one standard deviation. The lower concentration is due to the increased loss of BaP to the sediments. The steady state calculation shown in Figure 54 tends to support the higher partition coefficient of about 10^5 which is the order obtained directly from the field data. It should, of course, be recalled that the loading estimate is subject to some considerable uncertainty as is the loss mechanisms of volatilization and photolysis. Nevertheless, the calculation tends to indicate that the estimate of the BaP partition coefficient obtained from the empirical relationships may be low by an order of magnitude and thus highlights the need to utilize the empirical relationships with caution.

Time Variable Calculations

Although the preceding steady state calculation provides important insight into the fate of BaP, it is recognized from the preceding work reported on in this report, that the time to reach the steady state values is long and that over a 20 year period for lakes such as Michigan, the resulting concentration is at about 75% of the ultimate steady state values. Therefore, a series of time variable calculations were also conducted with constant BaP loading as shown in Table 20 beginning at time $t = 0$ with zero initial conditions. The results at two levels of BaP partitioning are summarized in Table 22 and Figure 55.

As shown in Table 22, the lake to lake variation in BaP concentrations either in the water column or the sediment differs by less tha about a factor of two. The highest concentration of BaP in the surface sediments for $\pi = 10{,}000$ is in Saginaw Bay. It can also be noted in Table 22 and Figure 55 that at $\pi = 10{,}000$ ℓ/kg the comparison to the observed data is not satisfactory. Figure 55 shows that at $\pi = 10{,}000$ the surface sediment concentration for Lakes Michigan and Erie is about 45 ng/g(d) or about one order of magnitude lower than the observed data. These time variable results, therefore, are confirmatory of the previously discussed steady state calculations. Figure 56 shows the time history under the two partition coefficients. For $\pi = 10{,}000$ ℓ/kg, the water column and sediment are at about 80 and 60% of steady state respectively while for $\pi = 100{,}000$ ℓ/kg, the water column and sediment are at about 20% of steady state.

Figure 55 and Table 22 indicate that a more favorable (but not totally desirable) comparison to observed data is obtained at the higher BaP partition coefficient of 100,000 ℓ/kg. The results also indicate the need to determine the partition coefficient for BaP, as a representative PAH for Great Lakes solids concentrations. On the basis of this application of the physico-chemical model to BaP in the Great Lakes, it is concluded that:

(1) the estimate of the BaP partition coefficient obtained from published empirical relationships is probably low by about an order of magnitude for the Great Lakes system,

TABLE 22

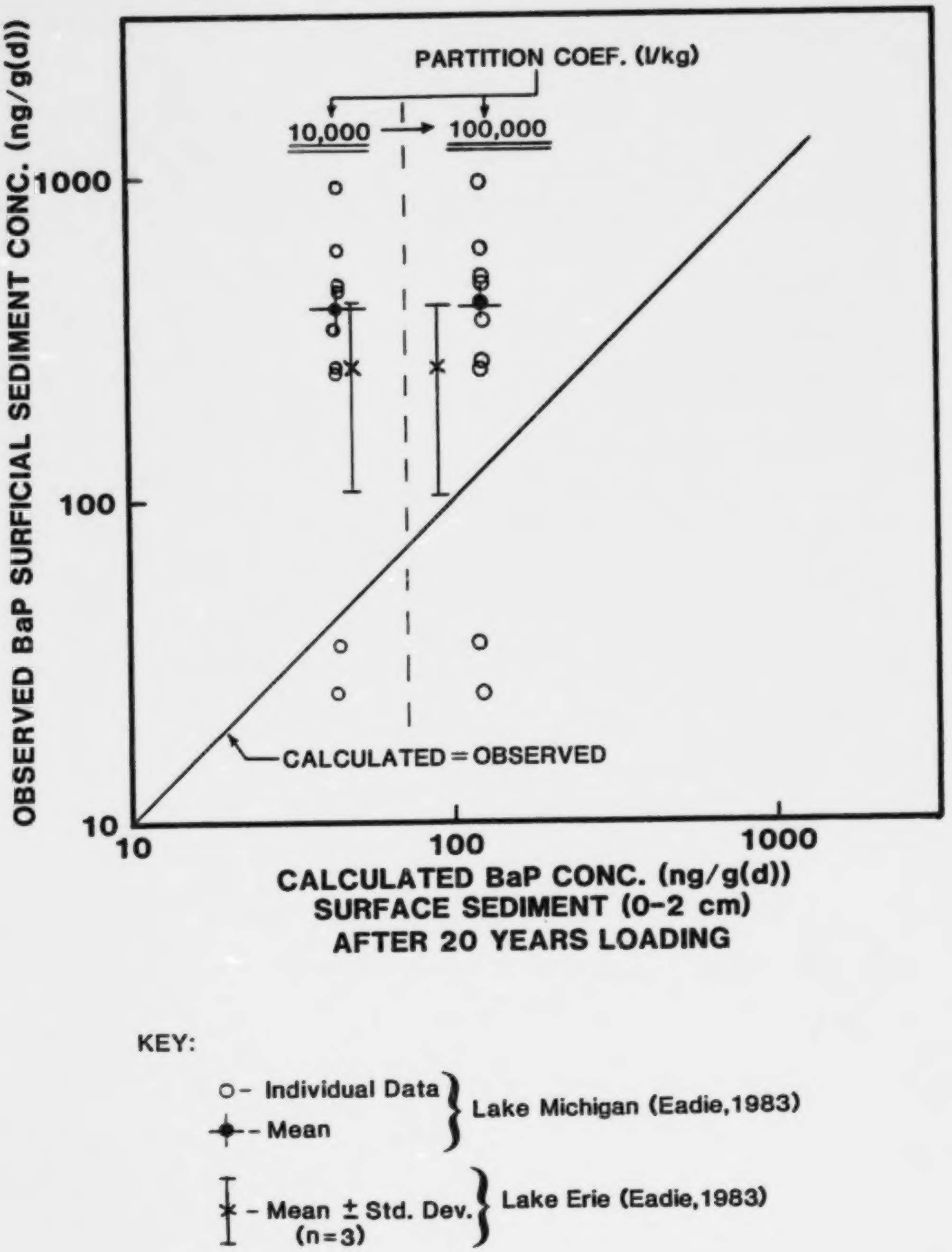
Comparison of Calculated and Observed BaP Under Different Solids Partition Assumptions

	Calculated Range of BaP Across All Lakes[a]		Observed Mean of BaP	Ref.
	π = 10,000 ℓ/kg	π = 100,000 ℓ/kg		
Total Water (conc.(ng/ℓ)	5-6	1-2	12 ± 8[b]	Eadie et al.(1983)
Surficial Sediment Conc. (ng/g(d))	38-60	46-133	Mich:480 ± 246(7)[c] Erie:255 ± 152(3) Sup.:28(1) Hur.:294(1) Ont.:306(1)	Eadie (1983)
Sediment Pore al.(1983) Water Conc(ng/ℓ)	3-5	0.5-1.3	850 ± 1260	Eadie et
Particulate Conc. in Water Column(ng/g(d))	46-64	46-165	Mich:200-400	Eadie (1983)

[a] After 20 years with loading of Table 20

[b] Mean ± Std. Dev.

[c] ( ) = No. of samples



55. Comparison between calculated surface sediment BaP concentration after 20 years and observed concentration.

(2) with an increased BaP partition coefficient and assuming loss due to volatilization, the physico-chemical toxic substances model of the Great Lakes approximate observed BaP water column and sediment data to order of magnitude,

(3) the model confirms that on a lake-wide scale, the principal external source of BaP is the atmosphere,

(4) for the larger lakes such as Michigan, the 50% response time of the lake to external loads is about 6-10 years for the water column-sediment system while for Lake Erie the response time is about two years,

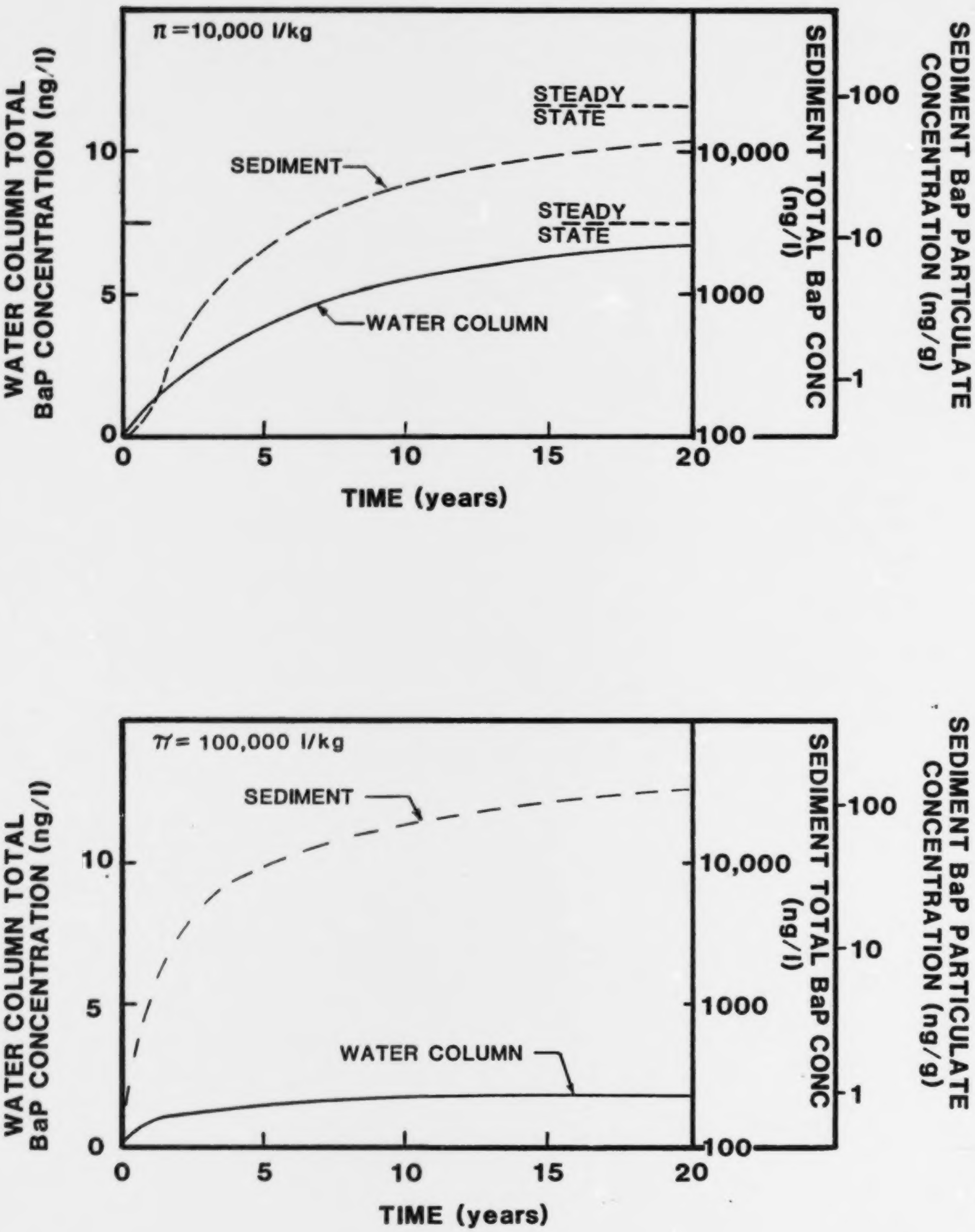
(5) lake to lake variations in BaP water column and sediment concentrations are less than a factor of two.

CADMIUM

Water Column and Sediment Data

The distribution of cadmium in the water column and sediments of the Great Lakes has been sampled for a number of years and a summary of much of the earlier data up to about 1977 is given by Konasewich, et al. (1978). As noted earlier in Section 5, Muhlbaier and Tisue (1980) have sampled for cadmium in southern Lake Michigan and have applied a simple mass balance model of cadmium for that basin. They point out that earlier measurements of cadmium in the water column (with a detection limit of usually 100 ng/ℓ) may be in significant error because of potential contamination during collection, handling and analysis. Muhlbaier and Tisue (1980) concluded that values of cadmium lower than 100 μg/ℓ are probably more representative of the actual concentrations. Indeed, in their work, they used an average from careful sample collection and analysis of 20 ng/ℓ. Thus, retrievals from the USEPA Storage and Retrieval System (STORET) for cadmium in all of the Lakes which were made as part of this research are suspect since concentrations for the years 1972-1978 are about one-two orders of magnitude higher than the much lower levels indicated by Muhlbaier and Tisue (1978). For Lake Ontario, (Nriaga), et al. (1981) reported mean values of about 50 ng/ℓ total cadmium for 1978 as opposed to reported concentrations of dissolved cadmium in STORET for 1971-1974 of about 200 ng/ℓ.

As a result, the STORET data base for water column cadmium concentrations were not used in this work, but reliance was placed on the more recent observations. Table 23 summarizes some of the data for the water column where the limit of detectability was below 100 ng/ℓ and where presumably special care was taken in sample analysis. As seen in Table 22, average water column data for Lakes Michigan and Ontario and Saginaw Bay are below 100 ng/ℓ although the variation is quite large. The lower cadmium concentration reported for 1978 should not necessarily be taken as evidence of a cadmium decline from the 1973-1975 reported values; again because of potential contamination problems. The data for Saginaw Bay when examined at a more detailed spatial level indicate that the waters of the outer Bay adjacent to Lake Huron and receiving inflow from Huron averaged about 80 ng/ℓ total cadmium during 1976.



56. Time variable BaP response in Lake Michigan under two partition coefficients with 20 year constant loading.

TABLE 23

Summary of Some Observed Cadmium Concentrations in the Great Lakes

	Total Concentrations Water Column (ng/ℓ)					Surface Sediment (μg/g(d))				
Lake	Date	Mean	Std. Dev.	# of Obs.	Ref.	Date	Mean	Std. Dev.	# of Obs.	Ref.
Superior						< 1976	1.2	0.8	404	(9)
							3.0	$0.7 \rightarrow 4.6^{(b)}$	40	(10)
Michigan	1973-75	70	70	60	(1)	1978	1.0	0.52	6	(4)
	1978	27	9.3	17	(3)	~ 1860	0.57	0.12	3	(4)
Huron						< 1976	1.4	3.9	197	(9)
						< 1760	1.0	-	-	(9)
Saginaw Bay	1976	59	~ 20-30	130	(5)					
Erie						1970	$5.4^{(c)}$	3.8	11	(9)
						1972	$0.7^{(b)}$	-	8	(8)
						~ 1920	$0.44^{(d)}$	$0.57^{(d)}$	6	(8)
Ontario	1969	90	-	~ 300	(7)					
	1973	160	-	1	(1)	1978	5.4	0.6	3	(2)
	1978	$50^{(a)}$	11	3	(2)					
"Background" Conc.										
Shale							0.3			(6)
Deep Sea Clays							0.43			
Granitic Rocks							0.13			

References:
- (1) Elzerman and Armstrong (1979)
- (2) Nriagu et al. (1981)
- (3) Muhlbaier & Tisue (1981)
- (4) Christensen & Chien (1981)
- (5) USEPA Grosse Ile (data communication) and Dolon & Bierman (1982)
- (6) Forstner and Wittmann (1979) from Turekian & Wedpohl (1961)
- (7) Chau et al. (1970)
- (8) Walters et al. (1974)
- (9) Konasewich et al. (1978)
- (10) Robbins & Edington (1976), quoted in Muhlbaier & Tisue (1981)

Notes:
- (a) "Labile" + particulate, May/June
- (b) Range
- (c) Western Basin
- (d) "Background" conc. at depths as calculated from (8).

Table 23 also shows some data on the cadmium concentration in the surface sediments of the Lakes although this summary does not include all data as compiled by Konasewich, et al. (1978). The range of sediment cadmium concentration is about 1-5 μg/g(d) with some tendency for the higher concentration to occur in the downstream lakes. "Background" sediment levels, i.e. cadmium concentration at depth equivalent to about 100 years ago for some Lake Michigan cases is about 0.4-0.5 μg/g(d) (Christensen and Chien, 1981). For Lake Erie, a background deep sediment concentration of 0.14 μg/g(d) has been reported (Forstner and Wittmann, 1979, p. 148) and Kemp, et al. (1974, 1976)(as reported in Forstner and Wittmann, 1979) indicated that the sediment cadmium enrichment factor (an aluminum normalized elemental ratio at the sediment surface to the Ambrosia horizon) was 4.0, 0.8 and 2.7 for the West, Central, and Eastern basins respectively.

For Lake Michigan, Elzerman, et al. (1979) reported particulate cadmium concentration in the water column of 5 μg/g(d) for a sample which is higher than the approximate 1 μg/g(d) in the surface sediment but because of the limited data it is not possible to conclude that this is a real difference. As noted earlier in Section 5 (Figure 11), the data of Nriaga, et al. (1982) indicated that to order of magnitude the surface sediment cadmium data and particulate water column data are equivalent although the concentrations do differ by a factor of about two with the particulate water column concentration higher than the surface sediment concentration.

Cadmium Loads

A variety of estimates of the external cadmium loads to the Great Lakes or to individual lakes or bays has been made. Recent examples include Casey, et al. (1977) for Lake Ontario, Muhlbaier and Tisue (1980) for Lake Michigan; Dolan and Bierman (1982) for Saginaw Bay and IJC (1980) for Great Lakes system. All of the load estimates indicate the significance of the atmospheric input of cadmium and the possibility that individual industrial point sources may discharge significant loads of cadmium to Great Lakes tributaries but that sampling is not yet definitive enough to provide detailed estimates of these sources. Indeed the range in atmospheric estimates is also quite large (as given below). Earlier attempts as part of this research to arrive at external loads of cadmium to the Great Lakes by carefully going through each major sector of a Great Lake basin were abandoned because of the wide variability in industrial load components.

Instead an approach similar to the load estimates for PCB was used; i.e. a range was assigned to each principal load component (atmospheric, tributary and municipal and industrial) and subsequent time variable model calculations were made for an upper and lower load estimate. A summary of the range of external loads is given in Table 24 and as seen for any given lake or region, the difference from low to high estimate is one-half to one order of magnitude. There is a general tendency for the loading to increase in the downstream direction with the highest areal loads in Western Lake Erie and Lake Ontario. This is principally due to the apparent increased atmospheric input and tributary loads for the downstream lakes.

TABLE 24

Summary of Contemporary External Cadmium Loads
(not including upstream loads)

Lake/Region	Atmospheric 1) mt/yr	Tributary 3) mt/yr	Mun. + Ind. 4) (mt/yr)	Total mt/yr	Total g/km^2-yr
Superior	41-108	13-126	0-0.3	54-234	651- 2823
Michigan	12-120	9-92	0.4-4	21-216	363- 3739
Huron	23-57	14-136	0.1-1	37-194	644- 3378
Sag. Bay 2)	3	2	0	5	1184
Erie- West	1-18	2-20	1-8	4-46	1321-15202
- Central	3-94	2-16	0.2-2	5-112	318- 7126
- East	1-38	1-12	0.1-0.5	2-51	320- 8155
Ontario	10-44	7-66	0.6-6	18-116	924- 5953

1) From Allen and Halley (1980)

2) From Dolan and Bierman (1982)

3) Assuming tributary flow at total cadmium conc. of 0.2-2.0 µg/ℓ

4) At 0.5-5.0 µg/ℓ for direct municipal point sources

Background Concentrations and Loads

An approximate calculation can be made of the background (i.e. conditions prior to any external anthropogenic input) cadmium concentrations and associated equivalent external loads using the steady state formulations discussed in Section 5. As shown in Table 22, the cadmium concentration of shale clays and rocks varies from about 0.1 to 0.4 μg/g(d). For the Great Lakes, however, the deep sediment cadmium concentration tends to be somewhat higher. For Lake Michigan, Christensen and Chieu (1981) show for three cases, a cadmium concentration corresponding to about the year 1860 of 0.57 μg/g(d). A "pre-colonial" value of 1.0 μg/g(d) for Lake Huron is tabulated in Konasewich, et al. (1978) from the work of Kemp and Thomas (1976). Walters, et al. (1974) provide data from which a mean background level (approximately for the year 1920) can be calculated at about 0.44 μg/g(d) with a standard deviation of 0.57 μg/g(d) and range of 0.0-1.5 μg/g(d). A range of 0.5-1.0 μg/g(d) was chosen to estimate background concentrations and loads.

Under equilibrium conditions and the assumptions discussed in Section 5, the concentration of particulate cadmium in the surface (background) sediment would be expected to be approximately equal to the particulate concentration in the water column (Eq. (6)). The total cadmium water concentration can then be computed from Eq. (19) and (15) as

$$c_T = \frac{rM}{f_p} \qquad (82)$$

The areal load can be computed from Eq. (61) with the net depositional rate, w_T given by Eq. (64). The results of the calculations are shown in Table 25.

As shown in that Table, the estimated background total cadmium concentration in th water column is about 4 ng/ℓ for the upper Lakes and Lake Ontario and 8-20 ng/ℓ for Lake Erie. The elevated concentration in Lake Erie is due to the increased solids concentration (and associated loading) into that Lake. The resulting estimated external background load, as shown, increases in the downstream direction to maximum levels in Lake Erie which are about an order of magnitude higher than the upper lakes. The last column of Table 25 indicates that the contemporary cadmium loads (Table 23) are about 10-50 times the background load for the Upper Lakes, Western Lake Erie, and Lake Ontario. Central and Eastern Lake Erie, however, have a lower bound of this ratio of less than one indicating present loads (at the lower bound) are approximately equal to historical background loads. This seems unlikely. The upper bound for these basins is about ten times background loads, a more plausible ratio from the sediment data (Table 23, Lake Erie).

Partition Coefficient

As previously discussed in Section 5 where a simple steady-state calculation of cadmium in Lake Michigan is discussed, Nriagu, et al. (1981) provide data for Lake Ontario from which a cadmium partition

TABLE 25

Estimate of Approximate Background Cadmium Concentration for Great Lakes

Lake/Region	Range in Total Background Water Col. Conc. (ng/ℓ)[1]	Background Conc. Used in Load Estimate (ng/ℓ)	Background Total Load (mt/yr)[2]	External Background Load (mt/yr)[3]	External Background Load g/km^2-yr	Ratio: Contemp. Load (Tab. 23) / Background Load
Superior	2.8- 5.6	4.0	6.1	6.1	37	18-76
Michigan	2.8- 5.6	4.0	3.1	3.1	54	7-69
Huron	2.8- 5.6	4.0	5.2	4.8	83	8-41
Sag. Bay	6.5-13.0	10.0	0.6	0.4	105	11
Erie-West	12.5-25.0	20.0	10.3	8.6	283	5-54
-Central	5.0-10.0	8.0	22.0	10.0	635	0.5-11
-East	5.0-10.0	8.0	12.0	4.7	754	0.4-11
Ontario	2.8- 5.6	4.0	4.0	2.6	132	7-45

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1) At assumed background sediment conc. of 0.5-1.0 µgcd/g(d); $r_s = r$ and Eq. (82) with π = 200,000 ℓ/kg.

2) Includes any upstream or exchange loads.

3) Not including any upstream or exchange loads.

coefficient of about 200,000 ℓ/kg can be calculated. HydroQual (1982) in a compilation of cadmium partition coefficients, calculated from available field data, determined the following relationship from regression analysis of data for lakes:

$$\pi = (3.52 \cdot 10^6)M^{-.9246} \qquad (83)$$

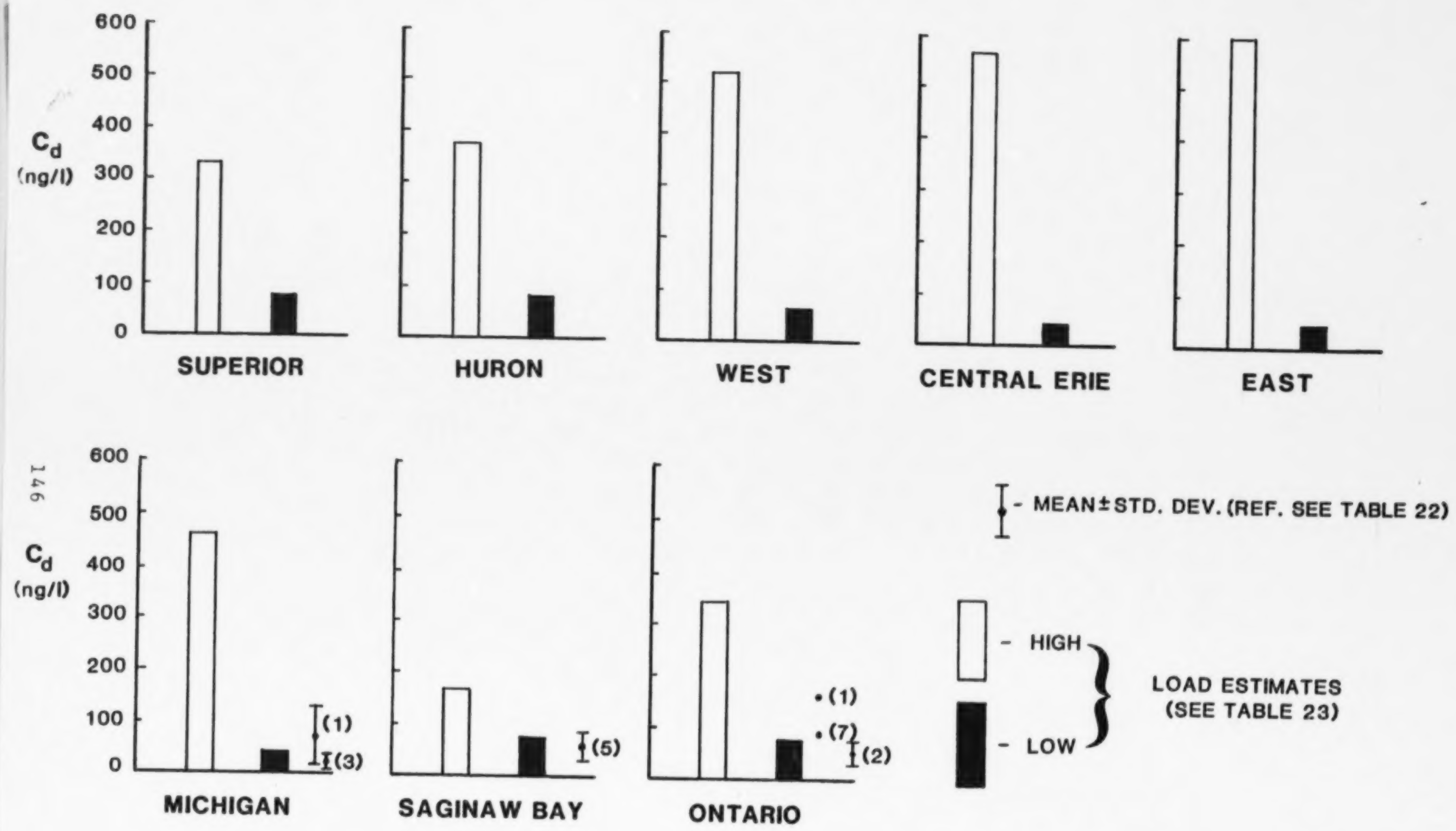
for a range of solids concentration of about 2-80 mg/ℓ. The ± one standard deviation error bars span about one order of magnitude and the standard deviation of the exponent is .0593. The data, however, show a clear decrease of the partition coefficient with solids concentration. In the model calculations, two conditions were examined: a) constant partitioning at 200,000 ℓ/kg and b) solids dependent partitioning according to Eq. (82) with associated sediment diffusion of dissolved cadmium.

Model Results

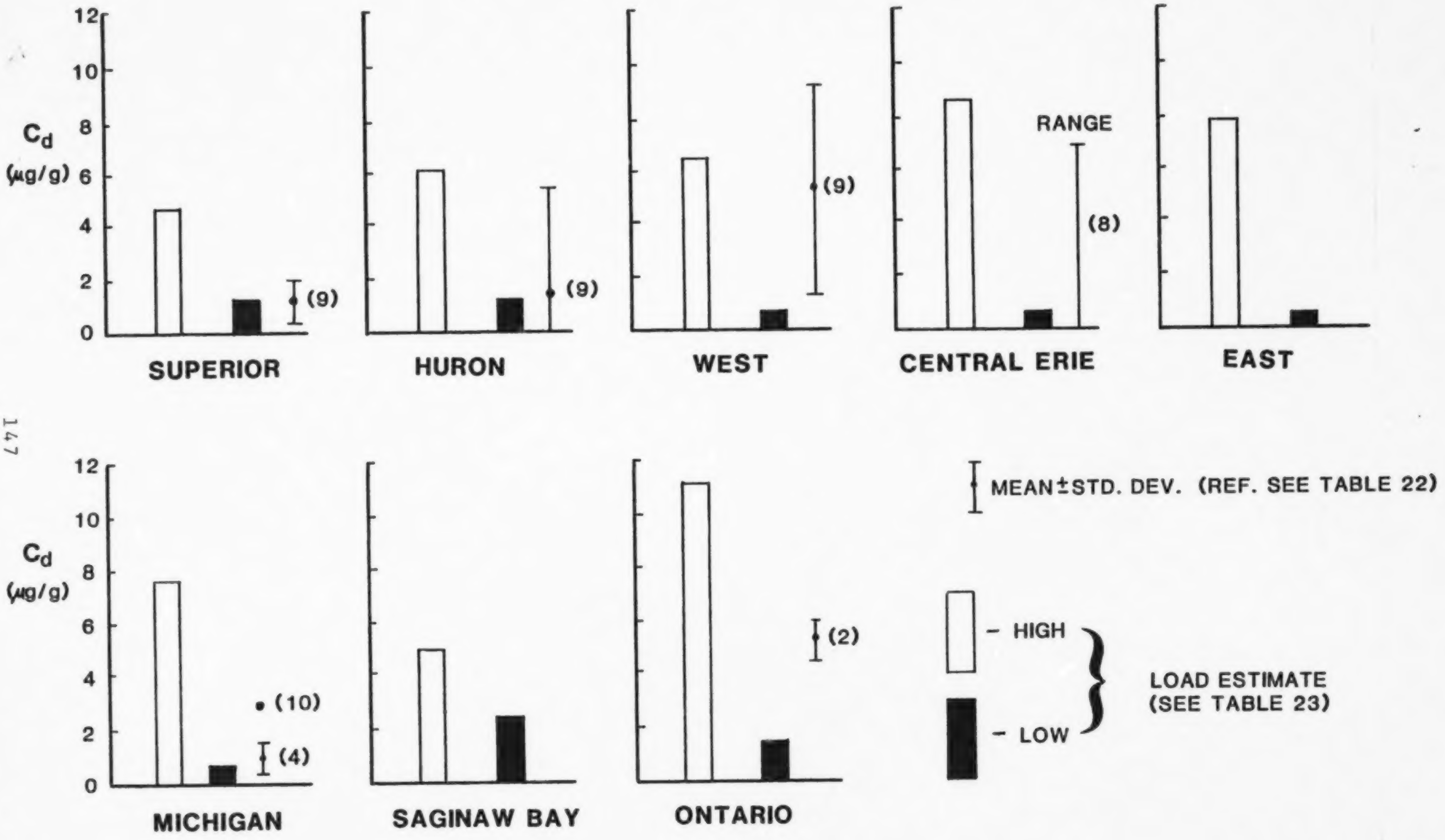
Model calculations were made using the low and high load estimate of Table 24 and two assumptions on the cadmium partition coefficient: a) variable partition with solids concentration as given in Eq. (83) and b) a constant partition coefficient of $2 \cdot 10^5$ ℓ/kg. Cadmium was assumed to be conservative kinetically. For all calculations, zero initial conditions were assumed and the loads were inputted as constant over time. It became apparent from initial runs that the time to steady state especially for the upper lakes is long so that the computation was carried out for a 100 year period. The computation therefore represents the response of the Great Lakes system to a constant loading and such loading can be viewed as a loading in addition to the background loading and cadmium concentrations shown in Table 25. If increased loading of cadmium is assumed to have begun in approximately the 1920's then the output from the model calculation at t = 50 years would be representative of the 1970's, the period during which some reliable data are available.

Figures 57 and 58 show the calculated lake to lake cadmium concentrations for the water column and surface sediment respectively under the high and low load estimate at t = 50 years. A solids-dependent partition coefficient is assumed. The comparison of the calculation to the limited water column and surface sediment data in Figure 57 shows that the high-load estimate substantially overestimates the concentration at 50 years for all lakes except Lake Erie. This is not surprising since it is unlikely that the upper bound of the cadmium load estimate has been persisting for the preceding 50 years. However the calculation does indicate that a loading close to the upper load estimate is not unreasonable for Lake Erie where the lower load estimate substantially underestimates the surface sediment concentration as shown in Figure 58. An estimate of the loading that is consistent with both the upper Lakes and Lake Erie is given below.

Figures 59 (low load estimate) and 60 (high load estimate) show the full 100 year calculation for Lake Michigan and central Lake Erie as illustrations. The sensitivity of the calculation to the assumptions in the partition coefficient is shown. As indicated, the effect of the solids dependent partition coefficient is to greatly increase the time

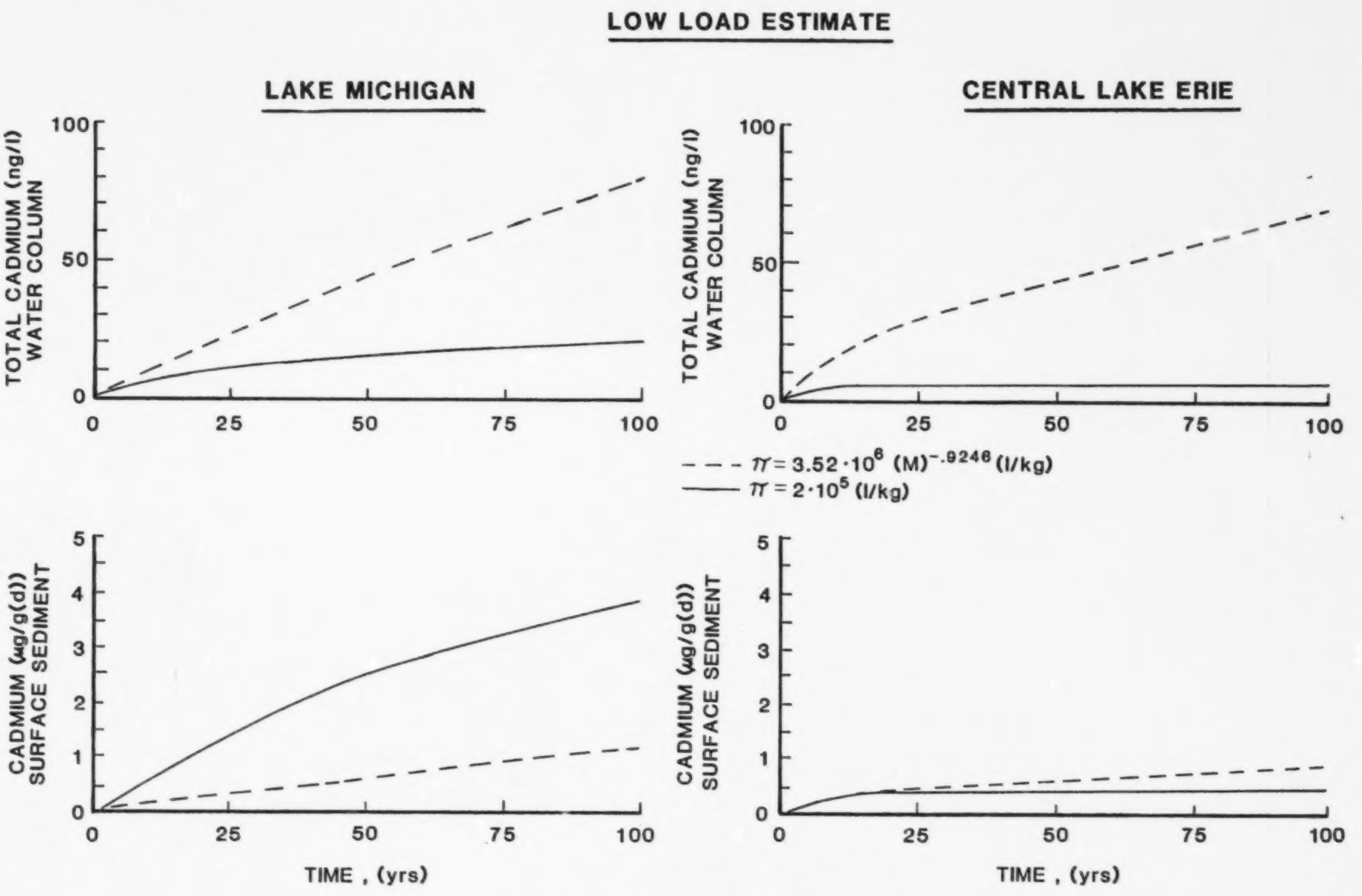


57. Calculated total cadmium concentration (mg/l) in water column at t = 50 years with partition coefficient as a function of solids concentration.



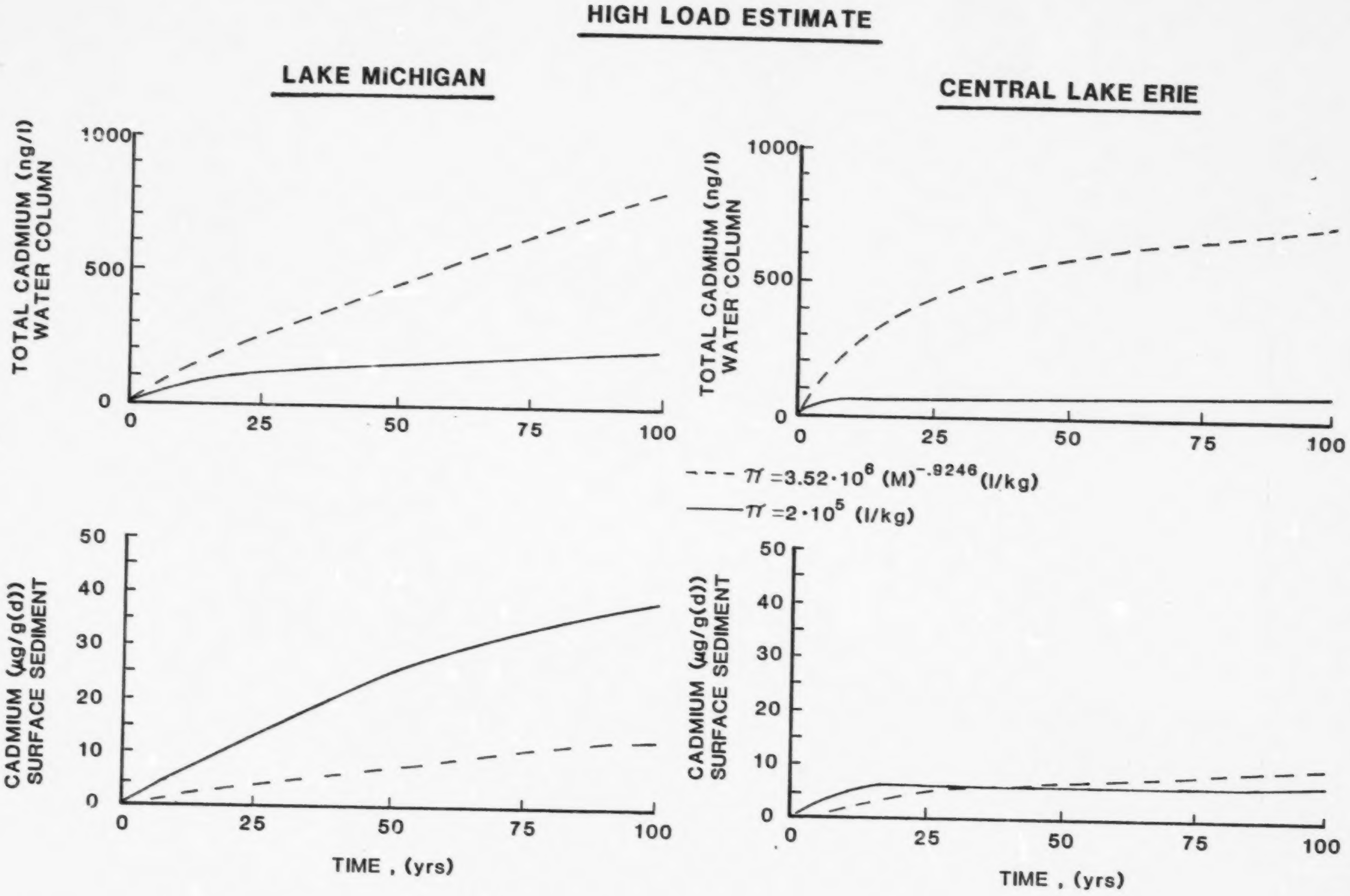
58. Calculated surface sediment concentration (μg/g(d)) at t = 50 years with partition coefficient as a function of solids concentration.

58



59. Comparison of calculated cadmium concentration under two assumptions on partition coefficient. Low load estimate.

59



60. Comparison of calculated cadmium concentration under two assumptions on partition coefficient. High load estimate.

to steady state as a result of the diffusive flux of cadmium from the sediment due to the lower partition coefficient. For Lake Michigan, the surface sediment concentration decreases with the variable partition coefficient but for Lake Erie the surface sediment concentration increases. This is similar to the response shown for PCB and discussed in Section 10. The continual increase in concentration for central Lake Erie reflects the non-equilibrium condition of the upstream Lakes.

If a constant partition coefficient is assumed (as in Muhlbaier and Tisue, 1981 and in Section 5 of this report, then it is seen that for the water column a steady state is reached in about 25 years for Lake Michigan and about 10 years for Lake Erie. A calculation then for Lake Michigan that attempts to calibrate to the mean concentration of 27 ng/ℓ (Table 22) then is simply a matter of estimating the approximate average load and may not reflect a non-steady state condition as concluded by Mulhbaier and Tisue (1981). However under a solids dependent partition coefficient for cadmium (which as noted earlier appears to be supported by field data for lakes, in general) the Great Lakes are not in equilibrium with the external load and for all practical purposes never reach a steady state condition. Clearly then, under this model construct, it is important to determine the solids dependence of cadmium for the range of solids encountered in the Great Lakes water column and sediments (i.e. 0.5-240,000 mg/ℓ). If however it is temporarily assumed that a solids dependent partition coefficient as given by Eq. (83) is applicable to the Great Lakes, then the system is not in equilibrium with respect to the external load.

Analysis of Model Results

Since the model equations are linear to the external load some further analysis of the Lake cadmium response can provide additional insight. Basically, a more appropriate estimate of the probable average load over the past 50 years can be made exactly for the upper Lakes (e.g. Michigan) and approximately for the lower Lakes (e.g. Erie). Let the rate (a) of cadmium response in the water column to external areal loading be given by

$$a(t) = \frac{c_T(t)}{W_a} \tag{84}$$

and also let Π be the ratio of the surface (0-2 cm) sediment cadmium concentration to the total water concentration, i.e. Eq. 69:

$$\Pi(t) = \frac{r(t)}{c_T(t)}$$

Figure 61 shows the load normalized water column response and the sediment/water column partition coefficient. For Lake Michigan as an upstream lake, the normalized response as required in the water column and sediment is linear to the load. Therefore, at 50 years, with a solid dependent partition coefficient, the normalized response is about 0.11 ng/ℓ ÷ g/km^2-yr. As noted, the difference in the partitioning between the surface sediment and water column under the two partitioning schemes is about an order of magnitude. Muhlbaier and Tisue (1981) using 20 ng/ℓ and 3 μg/g(d) concluded that Π = 150,000 ℓ/kg. However their data averaged 27 ng/ℓ and the sediment concentration may vary at least from 1-3 μg/g(d). At 30 ng/ℓ and 1 μg/g(d) Π = 33,000 or a factor of two above the variable partition coefficient case. The data therefore do not permit a distinction between the constant or variable partition assumption. However, since the compilation of data from other lakes resulting in Eq. (83) clearly indicates a solids dependence of the partition coefficient over the range of solids indicated, additional analyses are made on that assumption.

For central Lake Erie, because of the upstream load time variable behavior, the normalized response is dependent on the load level. (A more detailed analysis using individual load responses would provide exact load-independent normalized responses. However, time did not permit a full examination of the individual temporally variable responses). It is interesting to note however that the differences in the normalized response for a given partition coefficient assumption are not great. Also, the sediment/water column partitioning is essentially the same as for Lake Michigan. Figure 61 provides a basis therefore for estimating the water column and sediment response due to any load level constant in time.

If it is assumed, as indicated above, that the Lake system has been receiving an average increased load for about 50 years (i.e. a load in addition to the background load), then an estimate of that load can be made that is approximately consistent with the observed data of the 1970's. The results are shown in Table 26. As shown in this Table, either water column or sediment cadmium data were assigned to represent the condition of the 1970's. From the normalized response and the sediment/water column partition, either the water column or sediment concentration was computed and then the associated average 50 year load was calculated.

The calculations indicate that an average load of about 200-600 gCd/km^2-yr for the upper Lakes over the preceding 50 years results in a water column concentration of about 30 ng/ℓ and a surface sediment concentration of about 0.5 μg/g. Since background concentrations for these lakes are about 3-6 ng/ℓ and 0.5-1.0 μg/g, the total concentration is about 35-40 ng/ℓ and 1-1.5 μg/g(d). For Lake Michigan the water column concentration is higher than the 20 ng/ℓ used by Muhlbaier and Tisue (1981) and the sediment concentration is lower than the 3.0 μg/g(d) used in their work. The estimates in Table 26 however are within the range shown in Table 23. The loadings for the upper Lakes are below the lower loading level shown in Table 24. This reflects the fact that the loadings of Table 24 are estimates of contemporary (e.g. 1970's) loading whereas the estimated loading of Table 26 represent an average loading condition for the preceding 50 years.

TABLE 26

Estimate of Preceding 50 Year Average Cadmium Loading
Consistent With Observed Data in 1970's
(Solids dependent partition coefficient)

Lake	a (ng/ℓ ÷ g/km^2-yr)(1)	Π(2) (ℓ/kg)	Assumed 1970's Concentration(3) Water Col. (ng/ℓ)	Assumed 1970's Concentration(3) Surface Sed. μg/g	Calculated Water Col. (ng/ℓ)	Calculated Surface Sed. μg/g	Approximate Average 50 Year Load g/km^2-yr
Superior	0.114	15,000	-	0.5	33	-	290
Michigan	0.125	16,500	30	-	-	0.5	240
Huron	0.114(4)	15,500	-	0.5	33	-	290
Saginaw Bay	0.103(4)	30,000	60	-	-	1.8	580
Erie-West	0.041(4)	12,000	-	5.0	417	-	10,160
-Central	0.111(4)	15,000	-	3.5	233	-	2,100
-East	0.105(4)	13,000	-	3.5	269	-	2,560
Ontario	0.098(4)	17,000	75	-	-	1.3	765

(1) Calculated normalized response at 50 years = c_T/w_A

(2) Calculated surface/sediment water column partition coefficient

(3) Not including "background" concentration

(4) Average of high and low normalized response

For Lake Erie however the situation is different and average loadings as shown in Table 26 are towards the high end of the contemporary loading estimates. The calculated concentrations of 200-400 ng/ℓ are an order of magnitude higher than the upper Lakes and reflects the assumed higher sediment cadmium concentration for Lake Erie.

Figure 61 shows that for Lake Michigan and solids dependent partition coefficient that if the average load shown in Table 25 were to continue that the normalized response would increase to about 0.2 or about a 60% increase in the cadmium concentration over the next 50 years. The concentration however would still be less than 100 ng/ℓ, a level below any apparent toxic effects.

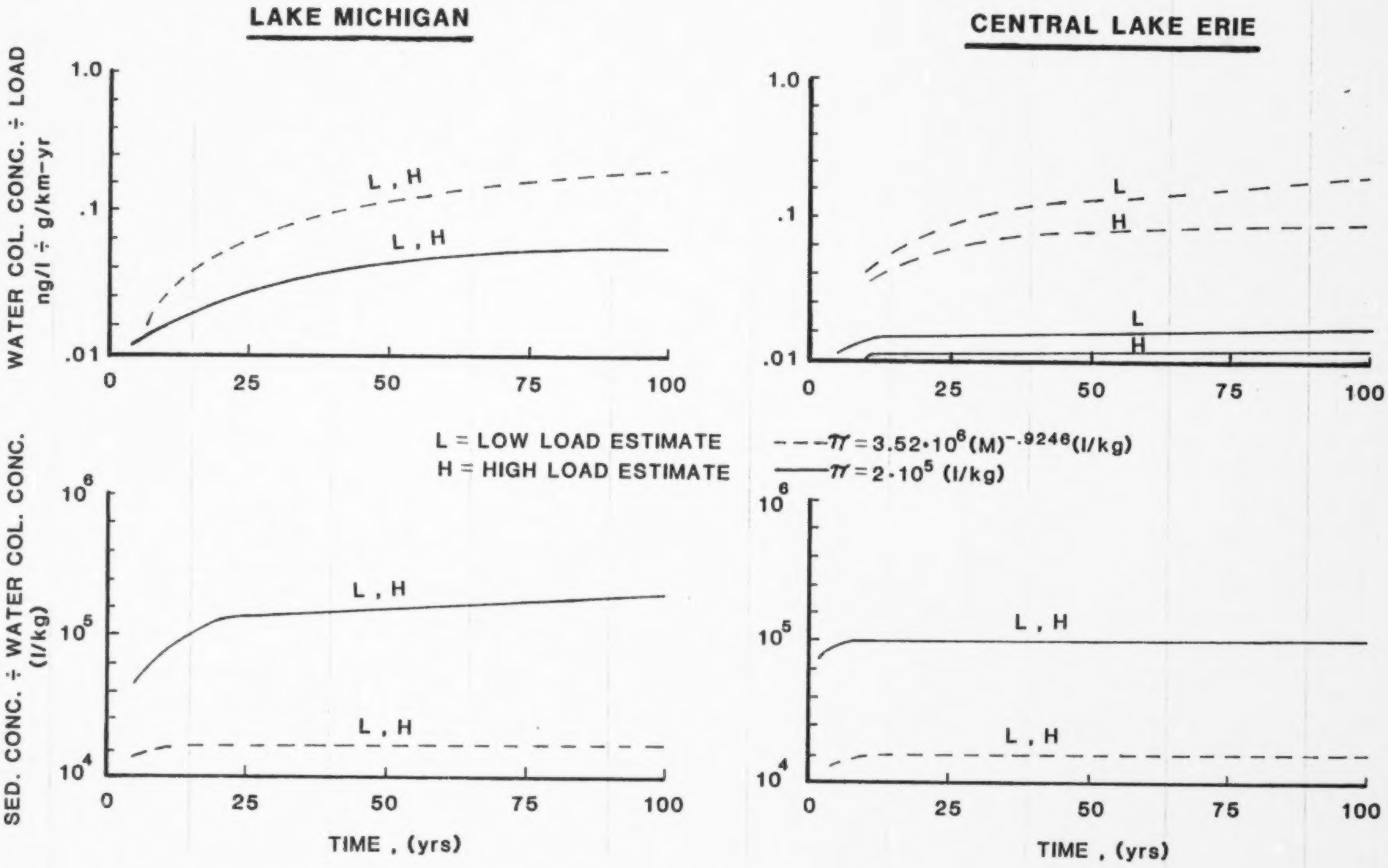
If however the load increases due to increased industrial usage and manufacture then the concentration may approach levels of several hundred ng/ℓ as projected by Muhlbaier and Tisue (1981). As such, cadmium should be monitored for the upper Lakes both in the water column, sediment and biota and periodic estimates should be made of the external cadmium load to the Lakes.

The computations also indicate that Lake Erie concentrations are about an order of magnitude higher than the upper Lakes. The estimates should be checked by a field sampling program to determine present cadmium concentrations in the water column and sediment. The calculations also indicate, in a manner similar to PCB, the significance of the partition assumption in the calculated interstitial cadmium concentrations. At a solids dependent partition coefficient, interstitial cadmium concentrations rise by about two-three orders of magnitude to levels of 10-100 μg/ℓ. It is of some importance then that the partition coefficient solids dependence be determined and more directly that measurements be made of the interstitial cadmium concentration in the sediment.

Conclusions

It is concluded from this application of the physico-chemical model to cadmium in the Great Lakes that

1) The degree of any dependence of the cadmium partition coefficient with solids has a marked effect on time to steady state and interstitial cadmium concentration.
2) Under a solids dependent cadmium partition assumption, the Great Lakes, especially the upper Lakes, do not reach a steady state condition after 100 years of constant loading.
3) Under a constant partition coefficient for cadmium, the Lakes do reach an equilibrium condition varying from about 25 years for Lake Michigan to 10 years for Lake Erie.
4) The concentration of cadmium in the Lakes would be expected to increase by about 60% over the next 50 years if the average cadmium loading for the preceding 50 years continues.
5) Based on assumed sediment cadmium concentrations for Lake Erie, it is estimated that the cadmium concentration in the water column is about an order of magnitude higher than the other Lakes.
6) If loads are projected to increase then cadmium concentrations in the Lake system may increase to levels of concern.



61. (Top) Calculated load normalized cadmium time variable response
(Bottom) Calculated sediment/water column partition coefficient time variable response.

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